

PATHWAYS OF

CHEMISTRY

VOL. I

D.P. GOEL & V.B AGRAWAL



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PATHWAYS OF CHEMISTRY

(Vol. I for Class XI)

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**Let us work as we pray, for indeed,
work is the body's best prayer to the Divine.**

**Remembering
Late Shri Hazari Lal Gupta,
who had appreciation for hard work.**

Preface

As we continue to teach, we continue to learn. We learn from our students as, each year, we help them in understanding their science courses. We also learn from our colleagues who have kindly offered many helpful suggestions in writing this book.

This book is designed for class XI students. It gathers together the requirements of the new syllabus introduced by the Central Board of Secondary Education, New Delhi. It takes into consideration not only the topics but the objectives set by the syllabus as well. It is an attempt to offer a simpler yet exhaustive exposition of the subject. It is an assurance to equip the students with all the informations on the topics.

In planning the book, we have adopted the following general principles:

- Each unit is prefaced with a list of learning objectives. The purpose of these objectives is to apprise the students of the scope of the unit.
- At the end of each unit, '**Self assessment questions**', have been included. It is an integral part of the book. Hence, the subject matter is presented in an objective question - answer format with the dual purpose of providing the subject matter to the students in a crisp form and of acquainting them with the possible questions on the matter.
- Numerous illustrations and diagrams have been embodied in the text. These present most of the topics in visual terms.
- At the end of each unit, a collection of '**Terminal questions**' have been provided, which cover the whole unit and whose aim is not merely to test the reader's knowledge, but also to promote understanding and to stimulate further thought.
- Presentation of the subject matter has been done in a sound, lucid and simple manner to help the students of all levels.
- The entire subject matter has been written in accordance with the recommendations made by the International Union of Pure and Applied Chemistry (IUPAC).

- Throughout the book, the emphasis has been put on the use of SI units to explain the values of physical quantities.
- Many solved numericals have been given to explain the subject matter and use of SI units.

Care has been taken over the layout of each page so as to present the subject matter vividly and attractively using figures, graphs and tables to reinforce the text. The terminal questions at the end of each unit vary in style and these may be used in tests, in class-room discussions, in revision or for home work.

Although considerable care has been taken in introducing the subject matter, yet the possibility of any error or ambiguity in matter/fact that may have found its way into the book in hand, cannot be ruled out.

We hope that the students will discover the beauty of science as they advance through the units of the book and achieve their intended goal.

We look forward to the comments and suggestions from readers for improvement.

We sincerely thank our friends; Dr. Mohan Katyal, Dr. K.L. Kapoor, Sh. I.C. Mathur, Dr. (Mrs) Veena Singhal and Dr. Radhey Mohan Singhal for their timely help and suggestions. Finally, we must thank our wives for their patience, help and encouragement at all times.

Diwali Day, 1989

D.P. Goel
V.B. Agrawal

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Atoms, Molecules and Chemical Arithmetic

.....hypotheses ought to be fited merely to explain properties of things and not attempt to predetermine them except in so far as they can be an aid to experiments.

ISSAC NEWTON

UNIT PREVIEW

- 1.1 Introduction
- 1.2 Measurement in chemistry
 - 1.2.2 Significant figures
 - 1.2.2 Significant figures
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 - 1.9.2 Significance of a chemical equation
 - 1.9.3 Calculations using chemical equations

Self assessment questions

Terminal questions

Answers to self assessment questions

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Determine the number of significant figures in any number
2. Determine the significant in an answer after an addition, subtraction, multiplication or division process
3. Express any number in scientific notation
4. Solve problems by the unit conversion method
5. Define matter
6. Classify and give examples of types of matter
7. Define element, compound and mixture
8. Explain the principle and working of different types of methods used in purifying (separating constituents from) a mixture
9. Test the purity of a substance
10. State and illustrate the laws of conservation of mass, definite composition, multiple proportions, and reciprocal proportions.
11. State the basic postulates the Dalton's atomic theory
12. Understand mole concept
13. Compute the number of moles in a given mass of an element or a compound
14. Compute from balanced chemical equations conversion factors for use in stoichiometric calculations
15. Solve different types of problems based on the balanced chemical equations
16. Calculate the volume of solutions needed for reactions

1.1 INTRODUCTION

Chemistry is a science that deals with the composition, structure and reactions of matter. The study of chemistry involves many complexities because of

1. the large varieties of matter that are known
2. the details of the structure of each type of matter, and
3. the limitless changes that the different types of matter undergo when interact with each other. The growth of chemistry is essentially dependent on the qualitative and quantitative observations about the matter. A scientific experiment involves making of observations, cataloguing them and ultimately use them in the solution of the problems. You are familiar with the experiments which determine volume, mass, length, temperature, etc.

1.2 MEASUREMENT IN CHEMISTRY

It is the pressure, volume, temperature, concentration and physical properties like density, amount of heat, etc., which are commonly measured during the course of chemical changes. The measured parameters are always compared with a standard measuring device, generally referred to as **unit of measurement**. For example, the temperature of a reaction is 25°C ; the concentration of a reactant is 2 moles per litre; the volume of a gas is 500 cm^3 etc. All these quantities consist of two parts - the number (25, 2 and 500) and the unit $^{\circ}\text{C}$, mol/L and cm^3 , respectively). All the measured properties are expressed in terms of a number and a unit.

1.2.1 Significant Figures

When we try to measure some properties like length of an object, volume of milk in a cup or weight of an apple, though the length of an object, volume of milk or weight of the apple are definite quantities, it is not possible to measure them exactly. There will always be some uncertainty in their measurements as these are measured by a **continuous variable**. When a measured or a calculated quantity is written down, some indication of the precision of the measurement must be given as well. Let an object be weighed on two different balances; on a crude platform balance it weighs 10.4g and on a sophisticated analytical balance it weighs 10.4206 g. We find that in the first case the precision is ± 0.1 g whereas in the second case it is ± 0.0001 g. The number 10.4 is said to consist of **three significant figures**, whereas 10.4206 consists of **six significant figures**. To designate the number of significant figures in a quantity is to give an indication of the confidence with which the number is known. The greater is the number of significant figures used to express a quantity, the smaller is the uncertainty (and greater the precision) in its measurement.

For example, the height of a pole can be reported in three different ways: 210 cm, 210.0 cm, 210.00 cm. The three ways look equivalent. The number of significant figures in the three cases are 3, 4 and 5 respectively. In the first case (210 cm) the digits 2 and 1 are certain but 0 is uncertain; 0 only represents the best estimate, which may be off by ± 1 . In this case the measurement is done with a crude scale. In the second case (210.0 cm) the scale used is more precise as the estimate off is ± 0.1 and in the third case (210.00 cm) the scale for measurement is even more precise as the estimate off in this case is ± 0.01 .

It is important to note that the result of any measurement should reflect faithfully the precision of the measurement. To report more significant figures than possible to measure in a given situation is misleading; to report less significant figures is suppressing some information which can be useful.

The following rules are applicable in determining the number of significant figures in a number.

1. All non-zero digits are significant (i.e., 4.008, 15.018 and 1.0080)
2. Zeros placed between non-zero digits are significant (i.e., 2.008, 14.046 and 20.040)
3. Zeros at the end of a number to the right of the decimal point are significant (i.e., 16.080)
4. Zeros to the left of the first non-zero digit are not significant. The number 0.00030 has two significant figures.
5. Zeros appearing at the end of a number and to the left of the decimal point may or may not be significant. For example, the number 20,000 has one significant figure if written as 2×10^4 , two significant

figures if written as 2.0×10^4 and three significant figures if written as 2.00×10^4 .

From the above rules we find that the number of significant figures in 4.008, 15.018 and 10.070 are 4, 5 and 5, respectively. The number 0.00002 has one significant figure and the number 0.000020 has two significant figures.

1.2.2 Significant Figures in Calculations

While doing an arithmetic calculation precision can be neither gained nor lost. This is maintained by the following simple rule. "The result should carry as many significant figures as are of the least precisely known quantity involved in the calculation".

Exercise 1.1: Find the sum of 17.5 and 13.61

Solution: $17.5 + 13.61$ should be reported as 31.1 and not as 31.11.

Exercise 1.2: (i) Find the sum of 10 and 5.62

(ii) Subtract 3.168 from 7.73

Solution: (i) $10 + 5.62 = 16$

(ii) $7.73 - 3.168 = 4.56$

Exercise 1.3: Multiply $12.60 \times 13.80 \times 4.04$

Solution: $12.60 \times 13.80 \times 4.04 = 7.02 \times 10^2$

The answer should have three significant figures

1.2.3 Rounding Off

At times we find that the number of figures in the final results are many more than needed according to the criteria of significant figures. Thus, we can say that the desired result may be composed of significant and non-significant figures. In the final result, the non-significant digits are rounded off. The following rules are used in rounding off the non-significant digits.

1. If the non-significant digit is less than 5, the last significant digit remains the same.
2. If the non-significant digit is more than 5, the digit is dropped and the last significant digit is increased by 1.
3. If the non-significant digit is equal to 5, there are two rules. Out of these two, either of the rule should be followed consistently.
 - (i) Increase the significant digit by 1.
 - (ii) If the significant digit is even, leave it as such; if it is odd, increase it by 1 to make it even.

1.2.4 Scientific Notations

Very large and very small numbers are expressed using scientific notations based on the powers of ten. The following steps are necessary to convert a number into the scientific (exponential) notation.

1. Reset the decimal point so that there is a single digit (not zero) to its left, e.g.,

$$0.00038 = 0003.8$$

2. Count the number of digits between the original and new decimal point position to determine the magnitude of the exponent of 10. It is 4 in the above example.
3. Determine the sign of exponent of 10. If new decimal is right to the old one, it is negative and if new decimal is left to the old one, it is positive. For above example, it is negative. Thus, $0.00038 = 3.8 \times 10^{-4}$

Using the scientific notation, each number can be expressed as,

$$N \times 10^n$$

Where N is a number having single non-zero digit to the left of decimal point and n is an integer.

Exponential manipulations are done as follows:

- (i) In multiplication, add the exponents or powers of the numbers, e.g.,
 $10^4 \times 10^5 = 10^{4+5} = 10^9$
- (ii) In divisions, subtract the exponents, e.g.,
 $10^6 \div 10^4 = 10^{6-4} = 10^2$
- (iii) In taking roots, divide the exponent by root number, e.g.,
 $10^4 = 10^{4/2} = 10^2$
 $510^{10} = 10^{10/5} = 10^2$
- (iv) In raising the powers of exponents, multiply the exponent with the exponent, e.g.,
 $(10^2)^2 = 10^{2 \times 2} = 10^4$

1.3 UNITS

Most of the scientific measurements are now expressed in the metric system. However, till 1960, two systems of units were used—British system and metric system. In the British system, the units of mass, length and time were pound, foot and second. The metric system was developed in France during 1790-1797 and it was accepted worldwide. The metric system is a decimal system. The various units for a physical property are related by powers of ten. The different powers of ten are indicated by a prefix. The unit of length, mass and time in this system are the metre, gram and second respectively. However, 10^{-2}m is known as centimetre while 10^3m is known as kilometre. Table 1.1 gives the prefixes which are used for reducing or enlarging the size of a unit.

1.3.1 SI UNITS

The International System of Units (SI units) was adopted by the General Conference of Weights and Measures in 1960. This system is now used throughout the world. The SI unit system has 7 basic units.

The units of mass, length and time are quite familiar. We buy fruit or vegetables in kilograms, measure cloth and report distance in metres (or kilometres) and measure time in seconds (or minutes, hours). Apart from these basic units, in everyday experiments we need several other units, e.g., units of area, volume, density, pressure, force, speed etc. These units

are given in Table 1.3.

TABLE 1.1 : The standard prefixes for reducing or enlarging the size of any unit.

Multiple	Prefix	Symbol
10^{18}	exa	E
10^{15}	peta	P
10^{12}	tera	T
10^9	giga	G
10^6	mega	M
10^3	kilo	k
10^2	hecto	h
10	deka	da
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a

TABLE 1.2 : The seven basic SI units.

Quantity	Unit	Symbol
Length	metre	m
Mass	kilogram	kg
Time	second	s
Temperature	kelvin	K
Electric current	ampere	A
Luminous intensity	candela	cd
Amount of substance	mole	mol

TABLE 1.3: Some of the common derived units

Quantity	Definition of quantity	SI unit
Area	Length square	m^2
Volume	Length cube	m^3
Density	Mass per unit volume	kg/m^3
Pressure	Force per unit area	$kg/(ms^2)$ (=pascal, Pa)
Force	Mass \times acceleration	$kg\ m/s^2$ (=newton, N)
Energy	Force \times distance	$kg\ m^2/s^2$ (=joule, J)
Speed	Distance travelled per unit time	m/s
Acceleration	Speed changed per unit time	m/s^2
Concentration	Amount/volume	mol/m^3
Power	Energy/time	J/s
Quantity of electricity	Current \times time	As
Electric potential	Power/current	J/As

1.3.2 Dimensional Analysis

Scientific compilation and evaluation generally require conversion of one set of units to another. The dimensional analysis or conversion factors are used to modify data on a particular unit. This involves a very simple and logical method as illustrated below:

Step 1. Read the problem carefully including given units.

For example : What is equivalent of 225 cm in metres?

Step 2. Condense the problem to a simple equality, i.e.,

$$225 \text{ cm} = ? \text{ m}$$

Step 3. Determine what relationship will be needed.

In present case, we need

$$1 \text{ m} = 100 \text{ cm}$$

Step 4. Set up the conversion factors properly using unit factor method so that either of the side is dimensionless. Write down the units clearly

$$\text{e.g., } 1 = \frac{100 \text{ cm}}{1 \text{ m}} = \frac{1 \text{ m}}{100 \text{ cm}}$$

$$\text{In present case } 1 = \frac{1 \text{ m}}{100 \text{ cm}}$$

Step 5. Do the arithmetic involved

$$\begin{aligned} 1 \times 225 \text{ cm} &= \frac{1 \text{ m} \times 225 \text{ cm}}{100 \text{ cm}} \\ &= 2.25 \text{ m} \end{aligned}$$

Step 6. Finally check the unit. In present case, it is metre

Exercise 1.4 : Convert 15 min into seconds

Solution : 15 min = ? seconds

$$1 \text{ min} = 60 \text{ seconds}$$

$$1 = \frac{60 \text{ s}}{1 \text{ min}}$$

$$\begin{aligned} 1 \times 15 \text{ min} &= \frac{60 \text{ s}}{1 \text{ min}} \times 15 \text{ min} \\ &= 900 \text{ s} \end{aligned}$$

It is always advantageous to write the units clearly. In the above examples, units of cm and min cancel out in the numerator and denominator leaving behind unit of m and s, respectively. Suppose, we write wrong conversion factor, e.g.,

$$15 \text{ min} = 15 \text{ min} \times 1 = 15 \text{ min} \times \frac{1 \text{ min}}{60 \text{ s}}$$

$$= \frac{1}{4} \frac{\text{min}^2}{\text{s}}$$

The mistake will be spotted out immediately. It is important to know the unit conversion factors of the common units expressed in different systems. Some are given in Table 1.4.

TABLE 1.4 Units conversion factors

2.54 cm/in.	0.394 in./cm
453.6 g/lb	0.0022 lb/g
0.454 kg/lb	2.2 lb/kg
0.946 L/qt	1.057 qt/L
0.00254 m/in.	39.37 in./m
100 cm/m	0.01 m/cm
1000 m/km	0.001 km/m
1000 mL/L	0.001 L/mL
1000 g/kg	0.001 kg/g
1.6×10^{12} erg/eV	6.25×10^{11} eV/erg
2.39×10^{-4} cal/erg	4.18×10^7 erg/cal
10^{-4} cm/Å	10^8 Å/cm
10^7 erg/J	10^{-7} J/erg
1.66×10^{-24} g/amu	6.02×10^{23} amu/g
760 torr/atm	1.32×10^{-3} atm/torr
101.325 kPa/atm	9.87×10^{-3} atm/kPa

1.4 CHEMICAL CLASSIFICATION OF MATTER

Matter has different forms. There are different methods to classify them. The physical classification categorises matter into three different states : solid, liquid and gas. On the other hand chemical classification suggests that matter essentially exists as element, compound and mixture. Mixture has been considered homogeneous if it is made up of the same type of constituents throughout and heterogeneous if it is made of different types of constituents. Figure 1.1 gives an account of the different classifications in brief.

The present knowledge of science interprets nature in terms of energy and matter. Matter is anything that occupies space and has mass while energy is the capacity to do work. You are always surrounded by matter in the form of house, clothes, trees, vegetables, *etc.* and energy in the form of light, heat, sound, *etc.*

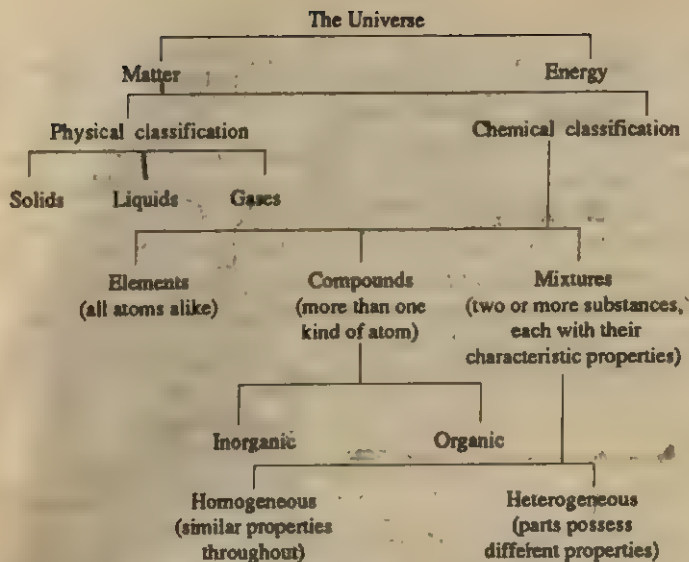


Fig. 1.1 Classification of matter

1.4.1 Mixtures, Compounds and Elements

Mixtures: Chemists always use physical and chemical properties to describe and identify a substance. Substances can be classified on the basis of their chemical nature. Most of the materials such as air, milk, gasoline and

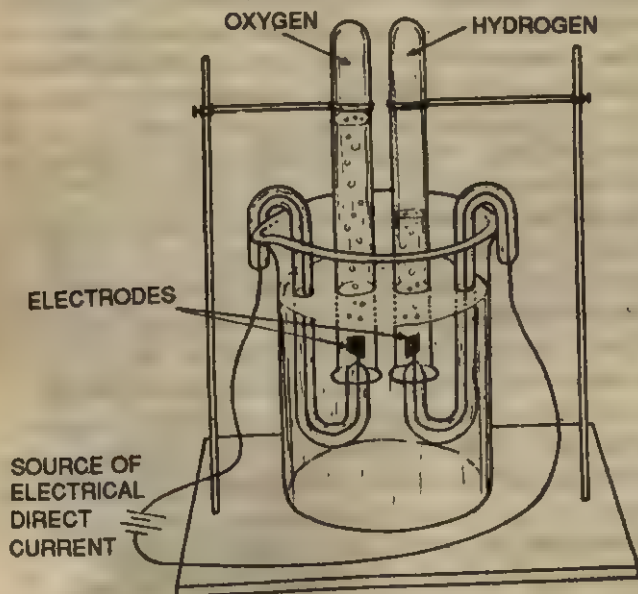


Fig. 1.2 Electrolysis of water forming hydrogen and oxygen (elements)

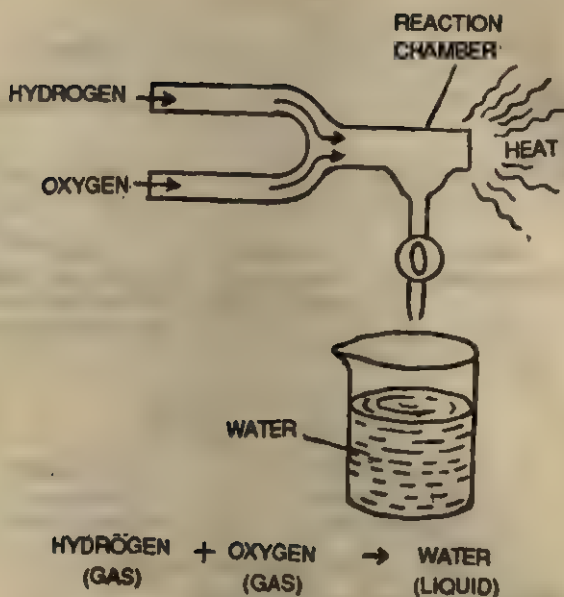


Fig.1.3 Synthesis of water (compound) from hydrogen and oxygen

steel are mixtures. Mixtures contain two or more distinct substances that can be physically separated from each other. Mixtures are broadly divided into two categories: heterogeneous and homogeneous. Heterogeneous mixtures are not uniform throughout rather different components of the mixture occupy distinct regions within the sample. A mixture of iron and sulphur is a heterogeneous mixture. The constituents of this mixture can be separated by simple methods. Homogeneous mixture has the same composition throughout the entire sample. Air, ink, drinking water and alcohol are examples of homogeneous mixtures.

Elements and Compounds: Water can be decomposed into hydrogen and oxygen by passing an electric current through it (Fig. 1.2). In this decomposition reaction, water is broken into two simpler substances. But these substances hydrogen and oxygen can never be broken apart into simpler substances. Those substances which cannot be broken down into other substances are called elements. Lead, iron, mercury and sulphur are examples of elements. Pure substances that can be decomposed or synthesized are compounds of their constituent elements. Water is a compound of hydrogen and oxygen; table salt is a compound of sodium and chlorine; and sugar is a compound of carbon, hydrogen and oxygen. In Fig. 1.3, water is synthesized from its constituent elements-hydrogen and oxygen.

So far 107 elements are known. Over 90 percent of the human body is composed mainly of four elements, i.e., oxygen, carbon, nitrogen and

hydrogen. Every element has been assigned a symbol for example, Cu for copper; Fe for iron; Na for sodium; Au for gold; and Ag for silver

Now we can easily reason out that substances may be classified into elements and compounds. A substance, say mercury, on heating produces a red substance which weighs more than that of pure mercury. On strong heating from this red substance, we again obtain the initial substance, i.e., mercury. The weight of mercury in the beginning and at the end is the same. The weight measurement method of lavoisier suggests that if on heating (or by similar physical and chemical methods) the weight of a substance changes, then the original substance is a compound otherwise it is an element.

Table 1.5 summarizes the differences between elements, compounds and mixtures.

TABLE 1.5 Differences between elements, compounds and mixtures

Elements	Compounds	Mixtures
1. Cannot be broken down into anything simpler.	1. Can be broken down into constituent elements.	1. Substances in a mixture can be present in any proportion.
2. Combine to form compounds	2. Have properties different from the constituent elements	2. Substances in a mixture retain their individual properties.
3. Composed of only one type of atoms.	3. Elements are present in a definite and fixed proportion by mass	

Experiment 1.1: Take a sample of water. Taste it. Taste water again after boiling it. You will notice the difference in taste. Now add sugar to it and taste it again. You will find it sweet. The sweetness of water increases as you add more and more amount of sugar into it. What happens when you add salt to water? Now the taste is salty. It is not only the taste which is affected, other properties of water like boiling point, freezing point, density, refractive index, etc., are also affected by the addition of salt (a soluble substance) to it.

From this experiment you can conclude that the properties of a mixture change as the relative amounts (composition) of constituents are varied.

As salt solution or a sugar solution is homogeneous as we cannot see the salt/sugar particles in the solution even under a microscope.

Homogeneous mixtures are formed in solid as well as in gas phase. Brass is a homogeneous solid solution of copper and zinc while air is a homogeneous gaseous solution of oxygen, nitrogen, carbon dioxide and water vapours.

In a heterogeneous mixture, the constituent substances do not have uniform distribution. The composition and properties of different samples of a heterogeneous mixture will be different. Concrete, milk, jam, jellies, air in a storm, etc., are some examples of heterogeneous mixtures. You will argue that milk is homogeneous. But the examination of milk under a microscope will reveal to you that small droplets of fat are suspended in the liquid. Table 1.6 lists various types of mixtures.

TABLE 1.6 Examples of different types of mixtures

Types of mixture	Homogeneous	Heterogeneous
Gas in gas	Air	
Gas in liquid	Aerated water ($\text{CO}_2 + \text{H}_2\text{O}$)	
Gas in solid	Hydrogen in palladium	
Liquid in gas	Moisture in air when we have mist	
Liquid in solid	Jellies	
Liquid in liquid	Alcohol in water	Oil-water
Solid in gas		Smoke (carbon in air)
Solid in solid	Alloys (brass, bronze)	Gun powder (potassium nitrate + sulphur + charcoal)
Solid in liquid	Salt in water	Sand + water

1.4.2 Separation of Constituents from a Mixture

There are different methods which can be used for the separation of constituents of a mixture. The choice of the method depends upon the nature of the constituents present into it. The melting point, boiling point, solubility, etc. are considered to be the basis for their separation. Some of the common methods used for this purpose are explained below. A few other methods will be discussed in Unit 18.

(i) Sedimentation and Decantation

When sand is added to water in a beaker it settles down at the bottom of the beaker (Fig 1.4). This is called **sedimentation**. The supernatant liquid is carefully poured into another beaker with the help of a glass rod as shown in Fig. 1.5. During this process the sand at the bottom is not disturbed. This process is called **decantation**. The process of sedimentation in conjunction with decantation is employed to separate a mixture of a liquid component and an insoluble solid component heavier than the liquid component.

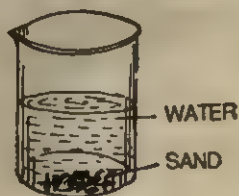


Fig. 1.4. Sedimentation

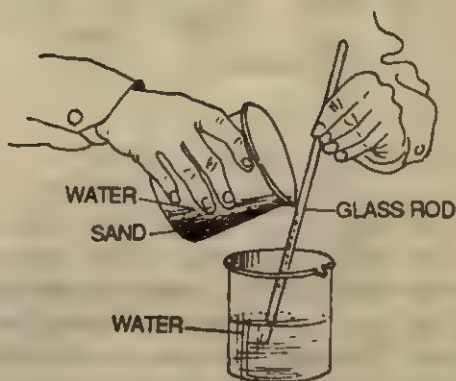
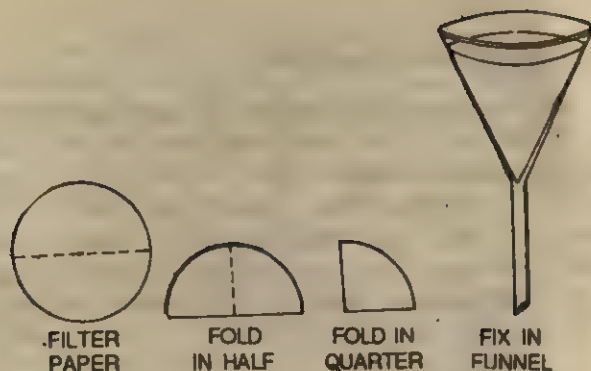


Fig. 1.5. Separation by decantation

(ii) Filtration

This method is employed to separate an insoluble component from a liquid. The mixture of insoluble component and the liquid is poured to a filter paper fixed in a funnel (Fig. 1.6). The residue (insoluble component) will remain on the filter paper and the clear liquid will pass through the filter paper and is collected in a beaker. The liquid so collected is called the **filtrate** (Fig. 1.6). This process is called **filtration**. The precipitate formed in a chemical reaction can be separated by filtration.



Folding and correct fixing of the filter paper in a funnel

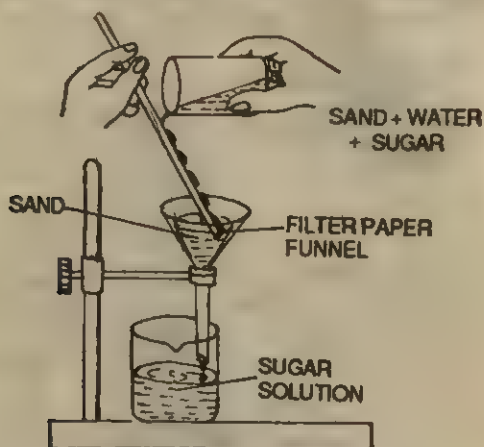


Fig. 1.6 Separation by filtration

This method could be used to separate the following mixtures.

(i) **Sugar and sand.** Sugar is soluble in water. On filtration sand will get collected on the filter paper. Sugar solution will pass through filter paper. From this solution sugar will crystallize out on concentrating the solution.

(ii) **Sugar and sulphur.** Sugar is soluble in water whereas sulphur is insoluble in water.

(iii) **Charcoal powder and sulphur.** Sulphur is soluble in carbon disulphide whereas charcoal powder is insoluble in carbon disulphide.

Thus by making use of the preferential solubility of one substance in a specific solvent, one can separate the two constituents of the mixture.

(iii) Evaporation

This method is employed for a mixture of miscible components when one of the components is non-volatile. When a mixture of sugar and water is heated slowly in a china dish kept on a wire gauze or sand bath as shown

in the Fig. 1.7, water evaporates and passes into the atmosphere. The residue (sugar) left in china dish can be collected. This method is called evaporation.

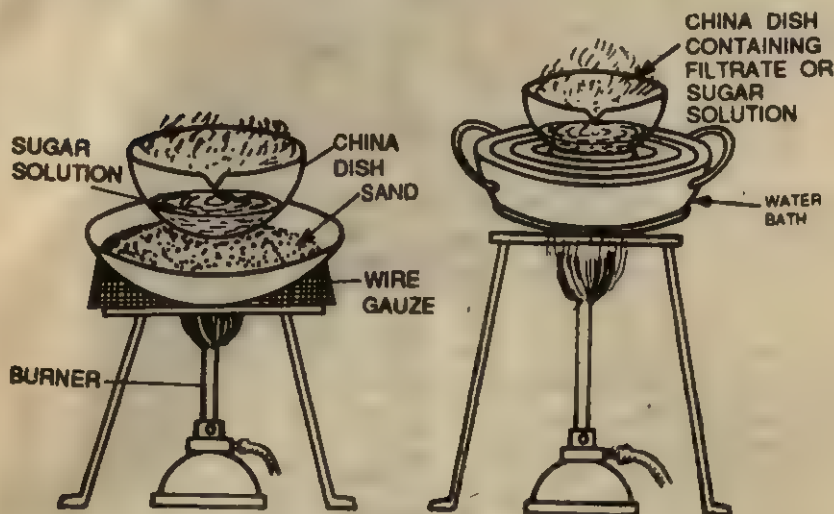


Fig. 1.7 Evaporation

(iv) Sublimation

This method is employed to separate a volatile component (like naphthalene, iodine, ammonium chloride, camphor, etc) from a mixture with non-volatile components. On heating, the volatile component in the mixture changes directly into vapours without liquefying. The vapours become solid on cooling. This process is called sublimation.



In a mixture of ammonium chloride and sodium chloride, ammonium chloride is a volatile component. This mixture is taken in a china dish and is covered with an inverted funnel as shown in Fig. 1.8. The stem of the funnel is plugged with cotton wool. On heating, the solid ammonium chloride is collected on the inner side of the funnel. The non-volatile sodium chloride is left on the dish.

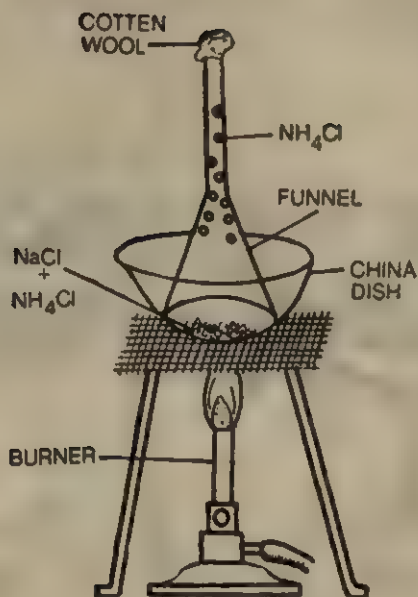


Fig. 1.8 Sublimation

(v) Distillation

Distillation is a process where a liquid on heating changes into vapours

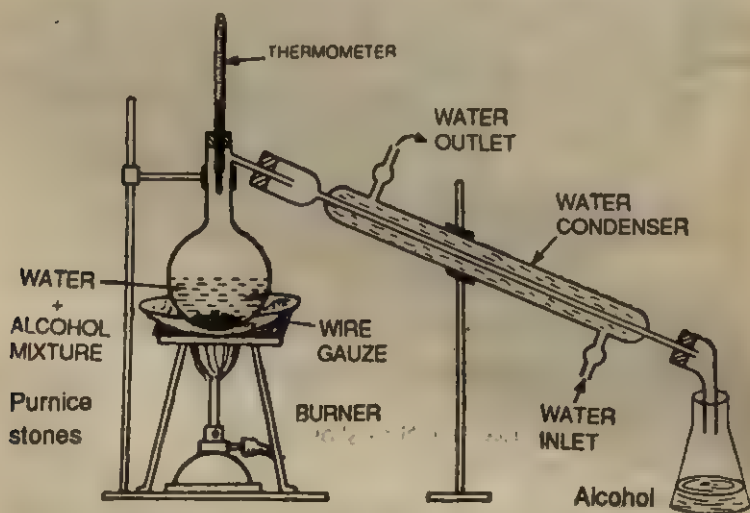


Fig. 1.9 Separation of a mixture by distillation
and then the vapours on cooling convert to liquid. This method is employed

to separate a mixture when both components are liquids or one is a soluble solid and the other is a liquid. Water and alcohol are completely miscible. Alcohol is a more volatile component. The mixture is taken in a round bottom flask which is fitted with a thermometer and a water condenser as shown in Fig. 1.9. On heating, the alcohol vapours pass through the condensing unit where these are cooled and collected in a receiver. Water remains as residue in the flask. Complete separation of water and alcohol is not possible by this method. A mixture of salt and water can also be separated by this method.

Simple distillation, described earlier is employed when the boiling points are far apart. When the components of a mixture boil within a narrow range of temperature, fractional distillation is used. (Unit 18)

(vi) Crystallization

Solid substances are more soluble in hot water than in cold water or some other solvent depending upon the nature of the substance. Therefore, if we cool down a saturated solution of a substance, it will slowly start separating and finally crystallize out. This method called crystallization is generally employed for the purification of the substances. Crystals that separate on cooling are filtered, washed and dried.

(vii) Separation by a magnet

When a magnet is rotated on mixture of iron filings and sulphur, the iron filings stick to the magnet and get separated from sulphur (Fig. 1.10). This method is used to separate the magnetically active component (e.g. iron) from a mixture.

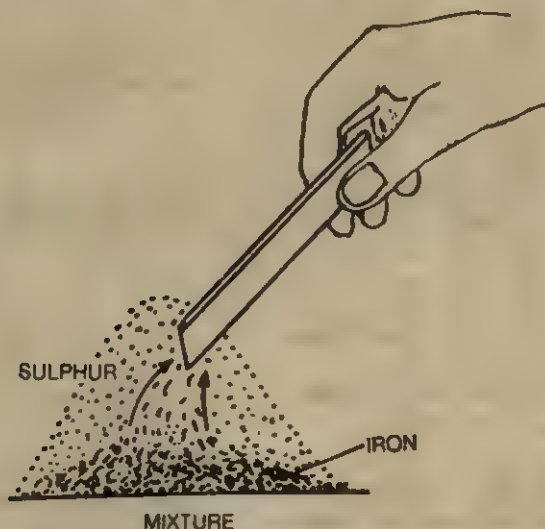


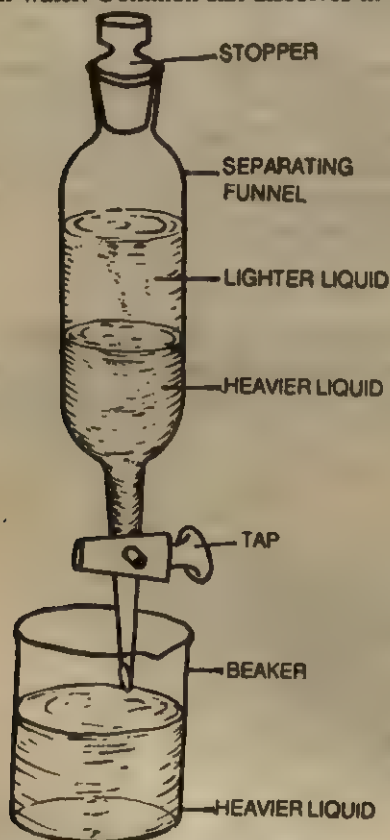
Fig. 1.10 Magnetic separation of a mixture of iron and sulphur

(viii) Separation by a Separating Funnel

A mixture of two immiscible liquids can be separated by this method. Oil and water do not mix but form separate layers. When these two immiscible liquids are taken in a separating funnel (Fig. 1.11), the heavier liquid forms the lower layer and the lighter liquid forms the upper layer. On opening the tap, the lower layer comes down first, followed by the upper layer. Mixture of benzene and water can also be separated by this method.

1.4.3 Separation of a few Mixtures

(i) **Mixture of common salt, sand and sulphur.** The mixture is treated with water. Common salt dissolves in water and is separated by filtration.



The residue contains sand and sulphur. This mixture of sand and sulphur is treated with CS_2 . Sulphur dissolves leaving sand undissolved. On filtration sand is obtained as a residue and sulphur in the filtrate. On evaporation, sulphur is obtained from the filtrate. The filtrate obtained earlier contains common salt. This is evaporated in a china dish. Common salt is left behind in the china dish.

Fig. 1.11 Separation of immiscible liquids by separating funnel

(ii) **Mixture containing sand, naphthalene and common salt.** Naphthalene being volatile is separated by sublimation. Mixture of sand and common salt is treated with water. Common salt dissolves in water and is

separated by filtration. Sand remains insoluble. Common salt is recovered from the filtrate on evaporation.

(iii) **Mixture containing kerosene oil, water and potassium nitrate.** Potassium nitrate is soluble in water. Kerosene oil and water are two immiscible liquids. Kerosene oil being lighter than water forms upper layer. It is separated from water layer using a separating funnel. The water layer contains potassium nitrate dissolved in it. On heating water evaporates and passes to the atmosphere. The residue (potassium nitrate) can be collected.

1.4.4 Purification of Substances

A pure substance is defined as any kind of matter of which all samples have the uniform composition and identical properties. For example, all samples of methanol contain exactly the same proportion of carbon, hydrogen and oxygen, regardless of the sources of the samples. All samples have the same boiling points. Pure substances may be elements or compounds. The components obtained by separation methods discussed in Section 1.4.2 are likely to contain other components (as impurities) in small quantities. The component can be purified by repeating the method of separation. The principles of both separation and purification methods are the same. Fractional distillation method is used to obtain pure liquids in case the boiling points of two liquids do not differ much. This technique will be discussed in detail in higher classes. If the liquid impurity has a boiling point nearly 40°C apart than that of the liquid to be purified, a simple distillation technique can be used. There are numerous other methods which are used for separation and purification of substances. Chromatography is based on the distribution/adsorption of a substance between a stationary and a moving phase (details are given in Unit 18). Separation methods based on differential electrical mobility (electrophoresis), sedimentation, velocity (ultracentrifugation), mass (mass spectrograph) and distribution between two immiscible liquids (countercurrent distribution) will be dealt in higher classes.

1.4.5 Test of Purity

The purity of a substance can be ascertained by determining its melting or boiling point. For a substance to be pure it must give that value of melting point or boiling point which is known to exist for pure substance. With impurities present, the value will vary from the standard value. Crystals also have definite shapes.

Melting point. Melting point of a substance is defined as the fixed temperature at which the solid changes into liquid. A pure substance has a sharp melting point. The apparatus used for the determination of the melting point is shown in Fig. 1.12. Finely powdered substance is taken in a small boiling.

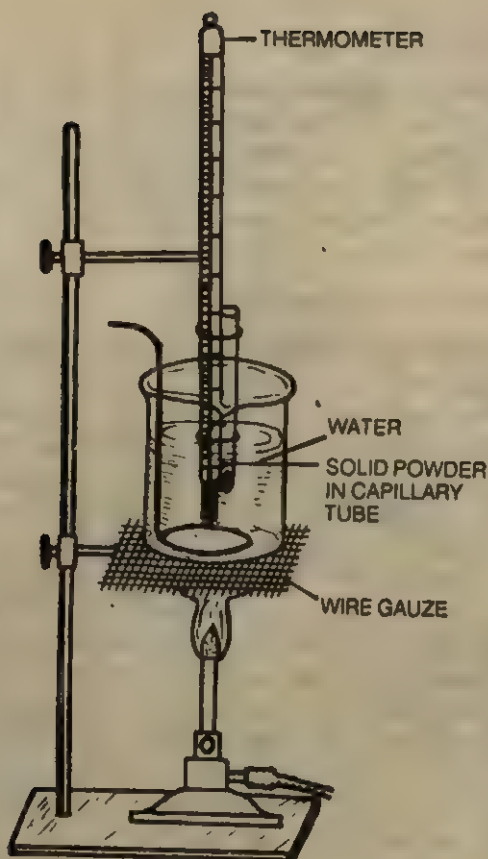


Fig. 1.12 Determination of melting point

tube or capillary tube. This is tied to a thermometer with a thread. The bulb of the thermometer is dipped into water taken in a beaker. Heat the water slowly to keep the temperature of water uniform throughout. When the opaque solid becomes transparent the temperature is noted. This is the melting point of the substance. This method is used to determine the melting points of substances which melt below 100°C . For determining the melting point of wax, a small boiling tube is used.

Boiling Point. The boiling point of a liquid is defined as the temperature at which the vapour pressure is equal to the atmospheric pressure. It must, however be noted that the boiling point is not as reliable test of purity as is the melting point for the solid. The apparatus used for boiling point determination is shown in Fig. 1.13. The liquid is taken in a small test tube which is attached to a thermometer, using a rubber band, in such a way so that the liquid stands near the thermometer bulb. A capillary tube sealed from

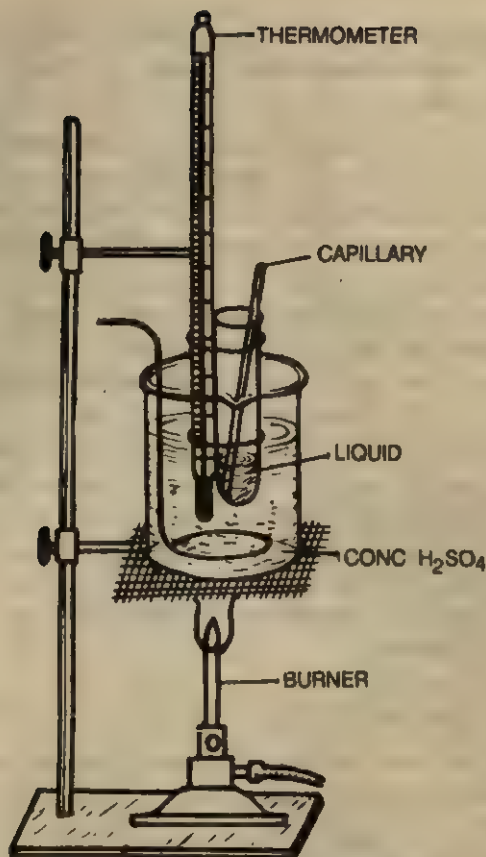


Fig. 1.13 Determination of boiling point

one end is put into it. The thermometer is then lowered into a beaker containing conc. H_2SO_4 and held in a position keeping half of the tube above the liquid. The liquid is now heated slowly. When the bubbles leave lower end of capillary in a rapid stream temperature is noted. The heating is stopped and the temperature at which the bubbles stop at the end of capillary is also noted. The mean of the two temperatures is taken which is the boiling point of the liquid.

Boiling points of organic liquids can also be determined by distillation of the liquid (Fig.1.9). For liquids boiling higher than 100°C , air condenser is used.

1.5 LAWS OF CHEMICAL COMBINATIONS

Chemical reactions always interest a chemist. Sometimes his wish is to cause a change and sometimes to prevent it. He always wished to understand and control the chemical changes that might occur. Based on experimental results he could formulate certain laws known as laws of chemical combinations. These laws govern a chemical reaction.

It is reasonably logical to accept that atoms of different elements have different masses. The process of combination can be looked in the form of a simple experiment.

Experiment 1.2 : Take balls of two different sizes containing hooks and pins arrangement so that these can be easily joined with each other. Let the mass of smaller size ball (X) be 5g each while that of bigger size (Y) be 10g each. Any number of balls can be joined with each other. Now observe the following :

1. Join one X and one Y ball and find out the mass. Compare it with the sum of the masses of the two balls.
2. Join one X and two Y balls and find out the mass again. Compare it with the sum of the masses of these balls.
3. Repeat step 2 by taking different numbers of X and Y balls.

What do you observe ? The mass of the combined balls is the same as the sum of the masses of the balls. What shall we observe if we do the above experiment in opposite direction ? Let us consider that we have a system consisting of one X and one Y ball. Its mass is 15g. Now, if we separate X from Y and find out the contribution of mass X and Y to XY. Then, we shall observe,

Mass contribution of ball X = $5/15 \times 100 = 33.3\%$

Mass contribution of ball Y = $10/15 \times 100 = 66.7\%$

Similar mass calculations for different chemical reactions invoked following general principles which are now known as laws of chemical combinations.

1.5.1 Law of Conservation of Mass

During a chemical change, the mass of the substances before and after the chemical reaction is always the same.

1.5.2 Law of Definite Proportions

In a given compound, the constituent elements are always combined in the same (definite) proportion by mass. This is regardless of the origin or mode of preparation of the compound. For example, carbon dioxide can be formed by different methods as combustion of carbon, decomposition of calcium carbonate, and neutralisation of sodium carbonate with an acid, but it always contains the masses of carbon and oxygen in the ratio 3:8.

1.5.3 Law of Multiple Proportions

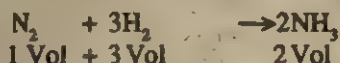
When two elements form more than one compound, the different masses of one element which combine with the same mass of the other element are in the ratio of small whole numbers. For example, nitrogen forms three oxides, viz., N_2O , NO and NO_2 . The masses of nitrogen which combine with 16g of oxygen are 28, 14 and 7g respectively which are in the ratio 4:2:1.

1.5.4 Law of Reciprocal Proportions

The mass ratio of two elements A and B combining with the fixed mass of an element C has the simple whole number ratio with the mass ratio in which A and B combine together. For example, mass ratio of oxygen and sulphur combining with 2g of hydrogen is 2. When oxygen and sulphur combine to give sulphur dioxide (SO_2), the mass ratio is 1. The two mass ratios have a simple whole number ratio 1:2.

1.5.5 Gay-Lussac's Law of Combining Volumes

In addition to mass relationships described above, Gay-Lussac observed that in homogeneous gaseous reactions, volumes of the reactants and products are related with each other by small integers under the similar conditions of temperature and pressure. For example,



In this reaction, N_2 and H_2 always combine in the volume ratio 1:3 and form 2 volumes of ammonia gas, *i.e.*, 1 litre of N_2 will combine with 3 litres of H_2 to give 2 litres of NH_3 under similar conditions of temperature and pressure.

1.6 DALTON'S ATOMIC THEORY

John Dalton (1804) proposed that all known properties of matter can be explained in terms of the simplest component of matter named as atom. According to Dalton's postulates

1. Atom is the smallest particle of an element.
2. Atom is tiny, hard, spherical and indivisible.
3. Atoms of an element are all alike but differ from the atoms of other elements.
4. Atoms of an element have fixed mass.

Dalton's postulate that elements consist of atoms which are identical to each other suggests that the element oxygen will consist of only a single type of particles called oxygen atoms. Similarly, element hydrogen, nitrogen, sodium, potassium, *etc.* are all made up of different types of identical atoms referred to hydrogen atoms, sodium atoms *etc.* The atoms of hydrogen are different from that of sodium. The other postulate of Dalton's atomic theory suggests that atoms of different elements have different properties. Thus, each types of atoms will have different physical and chemical properties which form the characteristics of the element. The indivisible nature of atoms is a direct consequence of the law of conservation of mass. During a chemical change, though it is possible for atoms to come closer and form a group of atoms held together by certain forces, it is quite improper that atoms of one kind are destroyed

and atoms of another kind are created. As we have seen that mercury combines with oxygen to give mercuric oxide which has different properties than mercury and oxygen, but when mercuric oxide is heated to get mercury again, the mercury atoms are all alike. If atoms were destroyed during a chemical change, the recovery of mercury atoms would not have been possible.

There are about 100 different types of atoms. When these atoms combine with each other according to laws of chemical combinations, they are capable of forming millions of compounds. A compound consists of group of atoms called molecules which are capable of independent existence.

The scientific advancement proved some of the Dalton's ideas to be incorrect. For example, the discovery of isotopes has shown that atoms of an element are not alike. Similarly, nuclear fission and fusion reactions had made it possible to convert one type of atom to another type. However, in the chemical reactions, the atom is still indestructible and Dalton's atomic theory is applicable to the chemical systems with slight modifications.

1.6.1 Atomic Mass

The atom is a very tiny particle which cannot be seen or subjected to physical investigation all alone. However, mass of an atom can be measured indirectly. For example take sufficient amount of an element which can be weighed. Now count the number of atoms in it. By dividing the mass with the number, one can find out the mass of a single atom. How to count the atoms? Even in a small amount of substance there are very large number of atoms. Unfortunately, there was no direct method available to count the number of atoms, therefore, this method was also not practical. However, the solution to this problem was suggested by Avogadro in 1811.

1.6.2 Avogadro's Law

The significance of Gay-Lussac's observation was later recognized by an Italian scientist, Amadeo Avogadro. He proposed that, "Equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules. Mathematically,

$$N = kV \text{ (At constant } T \text{ and } P)$$

here N = number of molecules

k = proportionality constant

V = volume of the gas

The most important application of Avogadro's law was in determining the relative atomic or molecular masses of the substances. For example, when hydrogen and oxygen gases are filled in the gas jars of equal volume at a particular temperature and pressure, it was noted that both have different masses. The repetition of this experiment taking different volumes re-

vealed that oxygen is 16 times heavier than hydrogen. Since equal volumes contain equal number of molecules, it may be concluded that one molecule of oxygen is 16 times heavier than a molecule of hydrogen. As it was later established that both hydrogen and oxygen are diatomic, the atoms of oxygen will be 16 times heavier than that of hydrogen. Using the same method, one can easily find out the relative atomic masses of all the elements. Now if we are able to find out the mass of one atom of any element, it will then be possible to predict the masses of the atoms of all elements.

Cannizzaro determined the relative atomic masses of several elements using the Avogadro's and Gay-Lussac's laws. The accurate determination of relative atomic masses showed that if hydrogen atomic mass is taken unity then the mass of oxygen atom is 15.88. The accurate determination of atomic masses is now done with the help of mass spectrometer in which atoms in the ionic form are passed through electric and magnetic fields where these are deflected at different angles according to their masses and collected at different points. The mass spectrometric studies revealed that all the elements consist of the atoms of more than one mass. The atoms of an element having different masses are known as isotopes.

1.6.3 Atomic Mass Unit (amu)

In the beginning, the unit for the atomic masses was taken from the mass of hydrogen atoms, because it was the lightest element available. But this resulted in the fractional value of atomic masses of large number of elements. Later it was observed that if oxygen is chosen as a unit of atomic mass and assigned it a value of 16, the atomic mass of most of the elements is a whole number.

In 1961, carbon-12 was chosen as a standard for atomic mass unit. (Carbon has three isotopes carbon-12, carbon-13 and carbon-14). In the modern atomic mass scale, the mass of carbon-12 isotope is taken exactly 12.0000 amu. The average atomic mass of carbon in a naturally occurring mixture is 12.011 amu. On this scale, the atomic mass of hydrogen is 1.008 amu while that of oxygen is 16.0 amu. Table 1.7 gives the average atomic masses of the elements on C-12 scale.

TABLE 1.7 Atomic masses of elements referred to $^{12}\text{C} = 12.0000$ amu

Element	Sym- bol	Atomic Number	Atomic (amu)	Element	Sym- bol	Atomic Number	Atomic (amu)
Actinium	Ac	89	(227)	Astatine	At	85	(210)
Aluminium	Al	13	27.0	Barium	Ba	56	137.3
Americium	Am	95	(243)	Berkelium	Bk	97	(245)
Antimony	Sb	51	121.8	Beryllium	Be	4	9.01
Argon	Ar	18	39.9	Bismuth	Bi	83	209.0
Arsenic	As	33	74.9	Boron	B	5	10.8

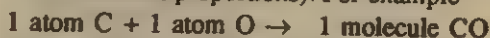
TABLE 1.7 Contd.

Element	Sym- bol	Atomic Number	Atomic (amu)	Element	Sym- bol	Atomic Number	Atomic (amu)
Bromine	Br	35	79.9	Nitrogen	N	7	14.0
Cadmium	Cd	48	112.4	Nobelium	No	102	(254)
Caesium	Cs	55	132.9	Osmium	Os	76	190.2
Calcium	Ca	20	40.1	Oxygen	O	8	16.0
Californi- um	Cf	98	(251)	Palladium	Pd	46	106.4
Carbon	C	6	12.0	Phosphor- us	P	15	31.0
Cerium	Ce	58	140.1	Platinum	Pt	78	195.1
Chlorine	Cl	17	35.5	Plutonium	Pu	94	(242)
Chromium	Cr	24	52.0	Polonium	Po	84	(210)
Cobalt	Co	27	58.9	Potassium	K	19	39.1
Copper	Cu	29	63.5	Praseodymium	Pr	59	140.9
Curium	Cm	96	(245)	Promethium	Pm	61	(145)
Dysprosium	Dy	66	162.5	Protactini- um	Pa	91	231.0
Einsteinium	Es	99	(254)	Radium	Ra	88	226.0
Erbium	Er	68	167.3	Radon	Rn	86	(222)
Europium	Eu	63	152.0	Rhenium	Re	75	186.2
Fermium	Fm	100	(254.0)	Rhodium	Rh	45	102.9
Fluorine	F	9	19.0	Rubidium	Rb	37	85.5
Francium	Fr	87	(223)	Ruthenium	Ru	44	101.1
Gadolinium	Gd	64	157.3	Samarium	Sm	62	150.4
Gallium	Ga	31	69.7	Scandium	Sc	21	45.0
Germanium	Ge	32	72.6	Selenium	Se	34	79.0
Gold	Au	79	197.0	Silicon	Si	14	28.1
Hafnium	Hf	72	178.5	Silver	Ag	47	107.9
Helium	He	2	4.00	Sodium	Na	11	23.0
Holmium	Hc	67	164.9	Strontium	Sr	38	87.6
Hydrogen	H	1	1.008	Sulphur	S	16	32.1
Indium	In	49	114.8	Tantalum	Ta	73	180.9
Iodine	I	53	126.9	Technetium	Tc	43	98.9
Iridium	Ir	77	192.2	Tellurium	Te	52	127.6
Iron	Fe	26	55.8	Terbium	Tb	65	158.9
Krypton	Kr	38	83.8	Thallium	Tl	81	204.4
Lanthanum	La	57	138.9	Thorium	Th	90	232.0
Lawrencium	Lr	103	(257)	Thulium	Tm	69	168.9
Lead	Pb	82	207.2	Tin	Sn	50	118.7
Lithium	Li	3	6.94	Titanium	Ti	22	47.9
Lutetium	Lu	71	175.0	Tungsten	W	74	183.8
Magnesium	Mg	12	24.3	Uranium	U	92	238.0
Manganese	Mn	25	54.9	Vanadium	V	23	50.9
Mendelevium	Md	101	(256)	Xenon	Xe	54	131.3
Mercury	Hg	80	200.6	Ytterbium	Yb	70	173.0
Molybdenum	Mo	42	95.9	Yttrium	Y	39	88.9
Neodymium	Nd	60	144.2	Zinc	Zn	30	65.4
Neon	Ne	10	20.2	Zirconium	Zr	40	91.2
Neptunium	Np	93	237.0				
Nickel	Ni	28	58.7				
Niobium	Nb	41	92.9				

Numbers in parenthesis give the mass number of the most stable isotope.

1.7 MOLE CONCEPT

Atoms or molecules are the basic units of all the chemical reactions. When atoms combine to form molecules they do so in a simple whole number ratio (law of constant proportions). For example



You know it is impossible to work with a single atom, therefore, this number is enlarged. In SI systems of units, the term mole (abbreviation - mol) is defined as the amount of a substance of a system containing as many elementary units as there are carbon atoms in 12 g of carbon-12. This number of elementary units is 6.023×10^{23} known as Avogadro's number. Therefore 1 mole contains $= 6.023 \times 10^{23}$ objects just as 1 dozen means 12 objects. This is to emphasize that the mole refers to a fixed number of any type of particles. A mole of hydrogen, a mole of helium, a mole of electrons, a mole of Na^+ ions, or a mole of sodium chloride always refers to Avogadro's number of atoms, electrons, ions or molecules.

In brief,

$$\begin{aligned} 1 \text{ mole} &= 6.023 \times 10^{23} \text{ particles} \\ &= \text{Mass in grams equal to atomic} \\ &\quad \text{or molecular mass of a substance} \\ &= 22.414 \text{ litres of a gas at STP} \end{aligned}$$

Molar mass is quite often used in chemical calculations. It is equal to the mass of the substance in grams which is numerically equal to its atomic mass in amu. The mole concept provides an easy method to calculate the absolute mass of an atom.

Exercise 1.5 Calculate the mass of a hydrogen atom and molecule in gram and kilogram (atomic mass of H = 1.008 amu).

Solution : We know, mass of 6.02×10^{23} atoms of hydrogen = 1.008 g

$$\begin{aligned} \text{Hence mass of 1 atom of hydrogen} &= \frac{1.008}{6.02 \times 10^{23}} \text{ g} \\ &= 1.67 \times 10^{-24} \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Mass of 1 atom of hydrogen in kg} &= \frac{1.008}{6.02 \times 10^{23} \times 10^3} \text{ kg} \\ &= 1.67 \times 10^{-27} \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{Mass of 1 molecule of hydrogen} &= \frac{2 \times 1.008}{6.02 \times 10^{23}} \text{ g} \\ &= 3.34 \times 10^{-24} \text{ g} \end{aligned}$$

$$\begin{aligned} \text{And mass of 1 molecule of hydrogen} &= \frac{2 \times 1.008}{6.02 \times 10^{23} \times 10^3} \text{ kg} \\ &= 3.34 \times 10^{-27} \text{ kg} \end{aligned}$$

Exercise 1.6 Calculate the mass of one atom of silver and iodine (atomic mass of silver = 107.9 amu and iodine = 126.9 amu).

Solution:

$$\text{Mass of 1 atom of silver} = \frac{107.9}{6.02 \times 10^{23}} \text{ g} = 17.9 \times 10^{-23} \text{ g}$$

$$\text{Mass of 1 atom of iodine} = \frac{126.9}{6.02 \times 10^{23}} \text{ g} = 21.1 \times 10^{-23} \text{ g}$$

Exercise 1.7 How many atoms are there in 6.495×10^{-6} g of potassium?

Solution: Atomic mass of potassium = 39.1 amu

39.1 g of potassium contain 6.02×10^{23} atoms

$$\therefore 6.495 \times 10^{-6} \text{ of potassium will contain} = \frac{6.02 \times 10^{23} \times 6.495 \times 10^{-6}}{39.1} \\ = 10^{18} \text{ atoms}$$

Exercise 1.8 Calculate the mass of one molecule and 1 mole of $\text{C}_2\text{H}_5\text{OH}$

Solution Mass of 1 molecule of $\text{C}_2\text{H}_5\text{OH} = (2 \times 12.0 + 6 \times 1.008 + 1 \times 16.0) \text{ amu}$
 $= 46.048 \text{ amu}$

Mass of 1 mole $\text{C}_2\text{H}_5\text{OH} = 46.048 \text{ g}$

1.8 CHEMICAL FORMULA

You are quite familiar about the chemical formulae of several substances, e.g. water is written as H_2O , hydrochloric acid as HCl and silver nitrate as AgNO_3 . Using the concept of valency, one can write chemical formula of any compound. But, for a moment if we are not aware of the valency and we simply know the weight composition of the constituent elements then can we write the formula or not? The weight calculation can provide some information about the chemical formula of a compound. In this context, we often use two terms - empirical formula and molecular formula. Empirical formula of a compound provides information about the relative number of different types of atoms, while molecular formula gives exact number of each type of atoms in a compound. For example, molecular formula of acetylene is C_2H_2 and benzene is C_6H_6 while empirical formula of both the compounds is CH .

The empirical formula of a compound can be determined from chemical analysis of the compound. In addition, atomic masses of the constituent elements must be known. The results of chemical analysis are generally expressed as weight percent. Oxygen percentage is usually not given explicitly but calculated by subtracting the sum of the percentages of other elements from 100. Following steps are performed systematically to obtain empirical formula of a compound.

1. Establish the percentage composition of all the elements of the compound.
2. Convert the percentage composition to molar composition. This is done by dividing the percent composition with the atomic mass of the corresponding element.
3. Convert molar composition into mole ratio. This is done by dividing molar compositions with the least number among them.
4. Remove fraction in mole ratio by dividing or multiplying with a suitable number - least mole ratio.
5. Write the empirical formula by writing symbol of the element and putting the whole number of mole ratio as a sub-script.

Exercise 1.9 An organic compound has 40 mass % carbon and 6.67 mass% hydrogen. Find out its empirical formula.

Solution:

Since the sum of the percent composition is not equal to 100, the compound contains oxygen also.

1. Hence mass percentage composition of elements is

$$C = 40 \quad H = 6.67 \quad O = 53.33$$

2. Mole composition of elements

$$C = \frac{40}{12} = 3.33 ; H = \frac{6.67}{1} = 6.67 ; O = \frac{53.33}{16} = 3.33$$

3. Mole ratio of elements

$$C = \frac{3.33}{3.33} = 1 ; H = \frac{6.67}{3.33} = 2 ; O = \frac{3.33}{3.33} = 1$$

4. As mole ratio is already in whole numbers, there is no need to remove fraction.

Hence empirical formula is CH_2O

To determine the molecular formula of a compound, following steps are required:

1. Do all the 5 steps needed to determine empirical formula
2. Find out the empirical formula mass of the compound by adding atomic masses of the elements as per formula
3. Determine the molecular mass of the compound.
4. Divide molecular mass by empirical formula mass and find out the nearest whole number.
5. Multiply the atoms of each element with the whole number obtained in step 4.

Exercise 1.10 If the molecular mass of the compound given in Exercise 1.9 is 60 amu, find out the molecular formula of the compound.

Solution : Empirical formula = CH_2O

$$\text{Empirical formula mass} = (12 + 2 + 16) \text{ amu} = 30 \text{ amu}$$

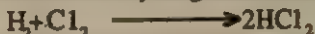
$$\text{Molecular mass} = 60 \text{ amu}$$

$$\text{Whole number} = \frac{60}{30} = 2$$

Hence, molecular formula is $C_2H_4O_2$

1.9 THE CHEMICAL EQUATION

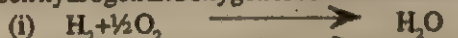
A chemical equation is the symbolic representation of a chemical reaction in terms of symbols and formulae of the reactants and products. For example, the reaction between hydrogen and chlorine can be written as



A chemical equation must represent a true chemical change and whenever it is written, it should also be balanced. For example, the equations



can be called chemical equations. By balancing of chemical equation, we mean that the number of atoms of each type must be the same on both sides (reactant as well as product sides) of the chemical equation. However, this situation can be achieved in different manners. For example, the reaction between hydrogen and oxygen to form water can be written as



1.9.1 The Principles to Write a Chemical Equation

1. Write down the symbol, formula of reactants and products in the form of their natural occurrence. For example hydrogen and oxygen should be shown as H_2 and O_2 , and not by simply H and O.
2. Reacting substances are written on left hand side and products on the right hand side separated by an arrow (\longrightarrow)
3. The balancing of equation is achieved by placing minimum possible whole numbers in front of each reactant and product.

Thus, equation (ii) is the chemical equation for the reaction. Some of the chemical equations for the reactions are given below:

- (i) Combustion of ethane,



- (ii) Hydrolysis of ethyl acetate



- (iii) Decomposition of potassium chlorate



- (iv) Formation of ammonia,

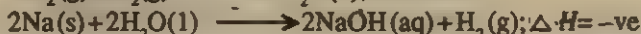


1.9.2 Significance of a Chemical Equation

1. A chemical equation provides informations about the reactants and the products.
2. From a thermochemical equation, the state of reactants and products, and the amount of heat evolved or absorbed can also be ascertained. In a thermochemical equation, the state of substances is denoted as

given below:

Solid = (s); liquid = (l), gas = (g) aqueous solution = (aq). If heat is absorbed it is shown as $\Delta H = +ve$ and heat evolved is shown as $\Delta H = -ve$. For example,



3. A chemical equation provides information about the mass, number, moles and volumes of reactants and products if the same is known for either of a reactant or a product, for example.



- From this equation we can say 2 moles of $KClO_3$, on decomposition, will give 2 moles of KCl and 3 moles of O_2
- 245.2g of $KClO_3$ will give 149.2g of KCl and 96g of O_2
- 245.2g of $KClO_3$ will give 149.2g of KCl and 67.2 litres of O_2 at STP
- $2 \times 6.02 \times 10^{23}$ molecules of $KClO_3$ will give $2 \times 6.02 \times 10^{23}$ molecules of KCl and $3 \times 6.02 \times 10^{23}$ molecules of O_2

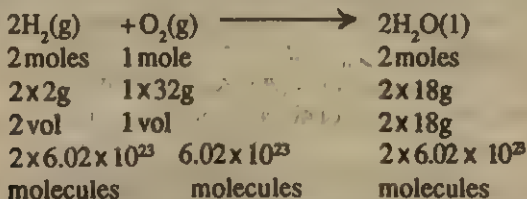
Thus, quantitative informations about the reactants and the products can be given by the use of a chemical equation.

1.9.3 Calculations Using Chemical Equations

The subject matter of obtaining quantitative information by the use of chemical equations is generally referred to as stoichiometry. The study of a chemical equation tells us

- The masses of other reactants or products when mass of atleast one component is given;
- the volumes of gaseous reactants or products when mass of atleast one component is given (or known);
- the volumes of the gaseous reactants or products when volume of atleast one gaseous component is given;
- The masses of the reactants or products when the volume of atleast one gaseous component is given.

One can compute the amount of substances and masses of the substances consumed or produced in a chemical reaction. For example,



Exercise 1.11 What mass of water (in gram) will be formed by the combination of 11.2 litres of oxygen (at STP) with excess of hydrogen?

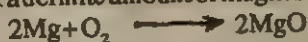
Solution: 11.2 litres of O_2 at STP = $(1/2)$ mole

Form the equation: $2H_2 + O_2 \longrightarrow 2H_2O$

1 mole of O_2 gives = 36 g of water

$(1/2)$ mole of O_2 will give = $36 \times 1/2 = 18$ g of H_2O

Exercise 1.12 In an experiment, 240g of magnesium oxide was obtained by burning of a definite amount of magnesium.



Find out the amounts and masses of magnesium and oxygen consumed, also calculate the volume of oxygen at standard temperature and pressure (STP).

Solution:

It is clear from the chemical equation that two moles of magnesium (Mg) react with one mole or 22.4 litres of oxygen (O_2) at STP.

The molecular weight of magnesium oxide (MgO) is 40 amu.

The amount of magnesium oxide in 240g is equal to $(240/40)$ moles or 6 moles. The amount of magnesium consumed will, thus, be equal to 6 moles and the amount of oxygen required will be equal to $\times 6 \frac{1}{2}$ moles or 3 moles.

Since the amount of magnesium consumed is 6 moles, therefore

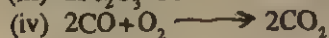
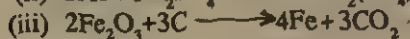
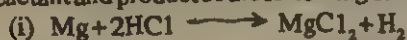
mass of magnesium consumed = $6 \times 24 = 144$ g

Similarly mass of oxygen consumed = $3 \times 32 = 96$ g

The volume of 3 moles of oxygen consumed = 3×22.4 or 67.2 litres at

STP

Exercise 1.13 What information do you draw about the amount of each reactant and product of the following chemical reactions?



Solution

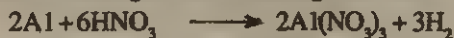
(i) One mole of magnesium (Mg) reacts with two moles of hydrochloric acid (HCl) to give one mole of magnesium chloride ($MgCl_2$) and one mole of hydrogen (H_2).

(ii) Two moles of aluminium (Al) react with three moles of sulphuric acid (H_2SO_4) to give one mole of aluminium sulphate ($Al_2(SO_4)_3$) and three moles of hydrogen (H_2).

(iii) Two moles of ferric (iron) oxide (Fe_2O_3) react with three moles of carbon (C) to give four moles of iron (Fe) and three moles of carbon dioxide (CO_2).

(iv) Two moles of carbon monoxide (CO) react with one mole of oxygen (O₂) to give two moles of carbon dioxide (CO₂)

Exercise 1.14 What mass of aluminium should react to give 71g of aluminium nitrate according to the following reaction?



Solution:

It is clear from the chemical equation that two moles of aluminium (Al) give two moles of aluminium nitrate, Al(NO₃)₃ or one mole of aluminium will give one mole of aluminium nitrate.

Mass of one mole of aluminium nitrate = 213 mol

Amount of aluminium nitrate = $71/213 = 1/3 = 0.33$ mole

The amount of aluminium required = 0.33 mole

Hence, the mass of aluminium = 27×0.33

= 9g

Exercise 1.15 Potassium chlorate (KClO₃) on heating gives,



What mass of potassium chlorate would be needed to obtain 240g of oxygen?

Solution:

Two moles of potassium chlorate give three moles of oxygen.

Amount of oxygen in 240g = $\frac{240}{32}$ moles

The amount of potassium chlorate needed = $\frac{240}{32} \times \frac{2}{3}$
= 5 mole

Mass of potassium chlorate required = 5×122.6
= 613 g

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

1.1 Put a (✓) mark against the most appropriate choice:

- (i) How many significant figures are there in the number 100.21?
(a) Two (b) Three (c) Four (d) Five
- (ii) The sum of 115.016, 12.0 and 3.4682 is
(a) 130 (b) 130.4 (c) 130.48 (d) 130.4842
- (iii) kg/cm³ is the unit of
(a) density (b) energy (c) pressure (d) volume
- (iv) Of the following masses, the one which is expressed to the nearest milligram is
(a) 16 g (b) 16.4 g (c) 16.428 g (d) 16.4284 g
- (v) Of the following numbers, the one with three significant figures is
(a) 13.05 (b) 0.0120 (c) 0.012 (d) 120.
- (vi) Which of the followings is a heterogeneous mixture
(a) Campa cola (b) vegetable soup (c) ice cube (d) tap water
- (vii) Which one of the following assumptions of Dalton's atomic theory is correct in most of the cases?
(a) Atoms are indivisible

- (iii) The mass of an individual carbon atom can be 12.0112 amu.
- (iv) Electrons and photons of light are examples of matter.
- (v) Different elements have atoms that differ in mass and size.
- (vi) Co is the element cobalt and CO is the compound carbon monoxide.
- (vii) $\text{CH}_4 + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$ is a balanced equation.
- (viii) Two elements sometimes form more than one compound.
- (ix) Temperature in $^{\circ}\text{C}$ = Temperature in K + 273.15.
- (x) At STP the volume of 1 mole of every gas equals 22400 millilitres.

1.4 Complete the sentences in column A with suitable choice given in column B.

Column A	Column B
(i) A mixture will be called homogeneous	(a) extremely small particles called atoms.
(ii) The properties of a compound are quite different	(b) decreases with the increase in pressure
(iii) Each element is composed of	(c) if its composition is the same throughout.
(iv) Heterogeneous materials	(d) from the properties of the constituent elements.
(v) At constant volume, pressure of a given quantity of a gas	(e) do not have fixed compositions
(vi) Molecules formed by the union of different kinds of atoms	(f) is a molecule of a compound.
(vii) One mole of a gas is equal to	(g) 22.4 litres at STP.
(viii) In equation $\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	(h) is directly proportional to absolute temperature.
(ix) Free movement of molecules in gaseous state	(i) results into homogeneity
(x) At constant temperature, the volume occupied by a definite amount of a gas	(j) 2 moles of water are obtained from 1 mole of methane.

SHORT ANSWER QUESTIONS

- 1.5 Mention the scientific laws for the following statements :
- (i) Equal volumes of all gases under the same conditions of temperature and pressure contain same number of molecules.
 - (ii) Matter is neither created nor destroyed in a chemical process.
- 1.6 Some pairs of compounds are listed below. From the information given about one of the compounds, supply the missing information about the other.
- (i) SnF_2 , stannous fluoride; SnCl_4 , _____
 - (ii) PbO , lead (II) oxide; _____, lead (IV) nitrate
 - (iii) CoSO_4 , Cobalt (II), sulphate; $\text{Co}_2(\text{SO}_4)_3$, _____
 - (iv) KIO_3 , _____; KIO_4 , potassium periodate
 - (v) FeCl_2 , iron (II) chloride; _____, iron (III) chloride
- 1.7 Supply the missing name or formula in each of the following :
- (i) CaF_2 , _____ (ii) $\text{Mg}(\text{ClO}_3)_2$, _____
 - (iii) _____ lithium aluminium hydride
 - (iv) NaH_2PO_4 , _____ (v) _____ potassium ferricyanide
- 1.8 Assume that the approximate diameter of the solar system, to the nearest million miles, is 7,300,000,000. Write this in scientific notation.

- (b) Atoms are indestructible
 (c) Atoms of elements combine in the ratios of small whole numbers to form compounds
 (d) All atoms of an element have the same mass.
- (viii) One mole of chlorine gas, Cl_2
 (a) weighs 35.5 g (b) weighs 6.02×10^{23} g
 (c) contains 6.02×10^{23} Cl atoms (d) contains 1.20×10^{24} Cl atoms
- (ix) Calcium cyanamide reacts with water and forms ammonia
 $\text{CaCN}_2 + 3\text{H}_2\text{O} \longrightarrow \text{CaCO}_3 + 2\text{NH}_3$
 when 1 mol of CaCN_2 reacts with 1 mol of water, the amount of ammonia formed is
 (a) $(1/2)$ mol (b) $(2/3)$ mol (c) $(1/3)$ mol (d) 2 mol
- (x) For the exact neutralization of 10.0 cm³ 0.1 M NaOH, sulphuric acid required is
 (a) 1.0 cm³ of 1 M H_2SO_4 (b) 10.0 cm³ of 0.1 M H_2SO_4
 (c) 10.0 cm³ of 0.5 M H_2SO_4 (d) 5 cm³ of 0.1 M H_2SO_4
- (xi) Which of the followings contains the greatest number of atoms?
 (a) 4 g of H (b) 100 g Pb (Atomic mass 207 amu)
 (c) 0.1 mol F_2 (Atomic mass 19 amu)
 (d) five billion N_2 molecules (Atomic mass 14 amu)
- (xii) Which of the followings contains the greatest mass of chlorine?
 (a) 0.1 mol Cl_2 (b) 10 g Cl_2 (c) 50 g KClO_3 (d) 10 g NaCl
- (xiii) What volume of NH_3 gas at STP would be needed to prepare 100 ml of 2.5 molar (2.5M) ammonium hydroxide solution?
 (a) 0.056L (b) 0.56L (c) 5.6L (d) 11.2L
- (xiv) 250 ml of 6 M HCl and 650 mL of 3M HCl were mixed together. What volume of water be added so that the normality of the final solution is 3N?
 (a) 75 mL (b) 100 mL (c) 135 mL (d) 250 mL
- (xv) When a certain volume of carbon monoxide is burnt, the same volume of carbon dioxide is obtained. This is because
 (a) oxygen combines chemically with carbon monoxide
 (b) the total number of atoms present on either side of the equation is the same
 (c) the number of molecules of carbon dioxide produced is the same as the number of molecules of carbon monoxide burnt
 (d) one mole of carbon monoxide and one mole of carbon dioxide contain the same number of atoms.

12 Fill in the blanks in the following sentences :

- (i) Ten grams when expressed to three significant figures will be written as _____
- (ii) Numerical answers resulting from calculations _____ precise than the data used in the calculations.
- (iii) There are _____ significant figures in 0.00100.
- (iv) 0.020 cm written in scientific notation is _____
- (v) 60 miles/h = _____ m/s
- (vi) One-twelfth of the mass of one atom of C-12 is known as _____
- (vii) Kelvin and Celsius scales are related as _____
- (viii) There are _____ H_2O molecules in a drop of water weighing 1 mg.
- (ix) The molecular mass of a certain compound of sulphur and oxygen is 80 amu. The possible simple formula of the compound would be _____
- (x) To obtain 0.235 mole tin from SnO_2 , the amount of H_2 required for reduction would be _____

13 Point out the correct statements of the following :

- (i) If a number is less than one, zeros following the decimal point are not significant figures.

Express the result of the following calculations to the appropriate number of significant figures :

- (i) $0.0123 - 0.000123$
- (ii) $(1.253/0.8694)(1.254) + 0.86$
- (iii) $\frac{4.579 \times 10^{-4}}{13}$
- (iv) $\frac{(6.9 - 4.973)(3.31 \times 10^{-2})}{7.34 \times 10^2}$

- 1.10 How many ammonia molecules are present in 0.060 mole of NH_3 ?
- 1.11 Determine the number of moles in each sample of elements given below :
 (a) 10.5 g iron nails (b) 56.0 g sample of nitrogen (N_2)
 (c) 720 g sample of sulphur.
- 1.12 What mass of CaF_2 should be dissolved in 250 g of H_2O to make a 1.0 molal solution?
- 1.13 A MgCl_2 solution has a density of 1.119 g/cm^3 and the percent of solute is 29.0% .
 Calculate the
 (i) molarity and (ii) molality of the solution
- 1.14 If one atom of an element X weighs $4.20 \times 10^{-22} \text{ g}$, find out the mass of this atom of X in amu.
- 1.15 When ferric oxide, Fe_2O_3 , is heated in an atmosphere of hydrogen gas, it is reduced to free iron,

$$\text{Fe}_2\text{O}_3 + 3\text{H}_2 \longrightarrow 2\text{Fe} + 3\text{H}_2\text{O}$$
 What amount of hydrogen is needed to reduce 265 g of Fe_2O_3 ?

TERMINAL QUESTIONS

- 1.1 Indicate how many significant figures there are in each of the following numbers
 (i) 3.704×10^{-54} (ii) 0.0036 (iii) 200.6 (iv) 600
 (Ans. (i) four (ii) two (iii) four (iv) ambiguous)

- 1.2 Round off the following to four significant figures
 (i) 16.223 (ii) 12.897
 (Ans. (i) 16.22 (ii) 12.90)

- 1.3 Convert
 (i) 12 yd^2 to m^2
 (ii) 30 miles/hour to cm/s
 (iii) 1.25 atm to torr
 (Ans. 10.03 m^2 , 1341 cm/s^{-1} , 950 torr)

The star nearest to earth is 2.6 light years away (the distance light travels in one year). If light travels at the rate of $3 \times 10^8 \text{ m/s}^{-1}$, how many Angstroms away is the nearest star?

(Ans. $2.6 \times 365 \times 24 \times 60 \times 60 \times 3 \times 10^8 \times 10^{10} \text{ \AA} = 2.5 \times 10^{23} \text{ \AA}$)

- 1.5 What amounts of hydrogen, sulphur and oxygen are there in 0.214 mole of sulphuric acid, H_2SO_4 ?
 (Ans. 0.428 mol H; 0.214 mole S, 0.856 mol O)

- 1.6 What is the empirical formula of a compound which on analysis gave 0.655 mole of A and 0.326 mole of B?
 (Ans. (A_2B))

- 1.7 18.6 g of iron is mixed with 0.250 mole of sulphur. Calculate
 (i) the mass in grams of a single iron atom
 (ii) the mass in grams of the sulphur in the mixture
 (iii) the total number of atoms in the mixture
 (Ans. (i) 9.26×10^{-23} g atom⁻¹
 (ii) 8.00 g (iii) 3.51×10^{23} atoms)
- 1.8 30.0 g of propanol, C_3H_7O , and 16.0 g of O_2 were placed in a container and ignited.
 (i) Write a balanced equation for the reaction
 (ii) What amount of CO_2 were produced?
 (iii) What mass of H_2O were formed?
 (iv) How many molecules of C_3H_7O were burned?
 (Ans. (ii) 0.335 mol CO_2 (iii) 7.99 g H_2O (iv) 6.69×10^{22} molecules)
- 1.9 What volume of 0.1060 M NaOH is required for the complete reaction of 25.0 mL of 0.1252 M HNO_3 ? (Ans. 29.5 ml)
- 1.10 A mixture of $MgCO_3$ and $Mg(OH)_2$ contains 26% $MgCO_3$ by mass. What mass of HCl are required to dissolve 14.0 g of this mixture? (Ans. 16.1 g HCl)

ANSWERS TO SELF ASSESSMENT QUESTIONS

- 1.1 (i) d (ii) b (iii) a (iv) c (v) b
 (vi) b (vii) c (viii) d (ix) b (x) d
 (xi) a (xii) c (xiii) c (xiv) d (xv) c
- 1.2 (i) 10.0 (ii) cannot be more (iii) three (iv) 2.0×10^{-3} cm
 (v) 26.8 m s^{-1} (vi) amu (vii) $K = 273.15 + t^\circ C$
 (viii) 3×10^{19} (ix) SO_3 (x) 0.47/mole
- 1.3 (i) T (ii) F (iii) F (iv) F (v) T
 (vi) T (vii) F (viii) T (ix) F (x) T
- 1.4 (i) c (ii) d (iii) a (iv) e (v) h
 (vi) f (vii) g (viii) j (ix) i (x) b
- 1.5 (i) Avogadro's law
 (ii) Law of conservation of mass
- 1.6 (i) stannic chloride (ii) $Pb(NO_3)_4$ (iii) Cobalt (III) sulphate
 (iv) potassium iodate (v) $FeCl_3$
- 1.7 (i) Calcium fluoride (ii) magnesium chlorite (iii) $LiAlH_4$
 (iv) sodium dihydrogen phosphate (v) $K_3[Fe(CN)_6]$
- 1.8 7.3×10^9
- 1.9 (i) 1.22×10^{-3} (ii) 2.7
 (iii) 3.5×10^{-5} (iv) 8.7×10^{-5}
- 1.10 3.6×10^{22}
- 1.11 (a) 0.188 moles (b) 4.00 moles of N
 (c) 22.5 moles
- 1.12 19.5 g CaF_2
- 1.13 (i) 3.42 M (ii) 4.30 m
- 1.14 253 amu
- 1.15 4.98 moles

UNIT 2

Elements Their Occurrence And Extraction

Who knows, whoever told, from whence this vast creation rose?

.....Rigveda

UNIT PREVIEW

- 2.1 Introduction
- 2.2 Elements
- 2.3 Earth as a source of elements
- 2.4 Elements in biology
- 2.5 Elements in sea
- 2.6 Extraction or metallurgy of metals
 - 2.6.1 Metallurgical processes
 - 2.6.2 Production of the concentrated ores
 - 2.6.3 Production of the metals
 - 2.6.4 Purification of the metals
- 2.7 Mineral wealth of India
- 2.8 Qualitative tests of metals
 - Self assessment questions
 - Terminal questions
 - Answers to self assessment questions

LEARNING OBJECTIVES

At the completion of this unit, you should be able to:

- 1. Comment on the distribution of chemical elements and their occurrence in the earth.
- 2. Emphasize the importance of chemistry in explaining the occurrence, distribution and composition of elements in the earth.
- 3. Comment on the various regions of earth.
- 4. Describe the various types of rocks.
- 5. Comment and describe the weathering process of igneous rock.
- 6. Describe the meaning of oceans - the great store house of chemicals".
- 7. Understand the importance of metals in life processes.
- 8. Understand the meaning of metallurgy.
- 9. Account for the sources of metals in the native and combined forms. .
- 10. Differentiate between a mineral and an ore.
- 11. Comment on the presence of metals as oxide, sulphide, carbonate, etc. in the nature.
- 12. Understand the working of various methods used for the purification and concentration of ores.
- 13. Comment on the suitability of a particular method used for the purification and concentration of ore.
- 14. Account the factors influencing the choice of methods used in reducing a metal ore.
- 15. Describe the following processes :
Cacination, roasting, aluminothermy, leaching, electrolytic reduction, smelting, electrolytic refining, bessemerization, etc.
- 16. Describe qualitative analysis of metals.

2.1 INTRODUCTION

Man has always been a curious animal. He expressed his curiosity in many ways - in exploration of the new world, in discovering Antarctica, in search of north pole, *etc.* Because of his curiosity he looked towards the vast sky and wondered about the universe. The true picture of this mysterious universe is still dim to him despite his sincere and painstaking efforts. The earth, he lives on, is only like a minute particle compared to the Milky way (one among thousands of the galaxies which populate the universe in and beyond the range of astronomical vision).

One currently popular theory for the origin and evolution of the universe to its present form begins with the "hot big bang" theory. According to this, all the matter and the radiant energy of the universe were initially compressed into a single object of immense density ("Primordial Egg") at a very high pressure and at a temperature of some trillions of degrees. At such high temperatures, the elements as such would not have existed. This supposedly small package was composed of subatomic and subnuclear particles (neutrons, protons, *etc.*). Owing to certain reasons, this primordial egg exploded, hurling the matter and the radiation outward in slowly decreasing expansion. This expansion led to rapidly dropping of temperature and this is the time when elements started forming. Thus, chemical elements are believed to be formed as a result of nuclear fusion of simple nuclear particles at very high temperature

(10^8K) first to heavier atomic nuclei as those of helium and then on to the heavier and more complex nuclei of light elements (Li, Be, B, *so on*). Be atoms, thus formed, bombarded the atoms of light elements and produced slow neutrons which are captured by the nuclei of other light elements and produced still more heavier elements. Thus, the elemental synthesis is believed to have originated through two main processes (i) fusion of protons, and (ii) neutron capture.

Further it was felt that the data available on the nuclear properties of the elements, could serve as a basis for theoretical consideration about the origin of matter in the universe. Accordingly cosmos appears to be a mixture of elements that are formed under different conditions by various types of nuclear reactions.

2.2 ELEMENTS

Nature is, somehow, very kind in giving us all the elements though in widely varying quantities. Of the 107 elements presently known, about 85 are obtained from natural sources and others are obtained from nuclear reactions. All materials found in earth are composed of these elements. Around 70 percent of the elements are metals.

Several of the metals are rare and have little practical value, but some metals are abundant, *e.g.*, Cu, Al, Ca, Fe, Na, Zn, Mg, and Ti. Our civilization is based upon all such metals. Metals are useful in varied

type of industries — automobiles, agricultural machinery and implements, aeroplanes, buildings, warships, ships, defence equipments, *etc.* Metals play a vital role as catalysts in certain chemical processes, *e.g.*, hydrogenation of vegetable oils, manufacture of ammonia, sulphuric acid, nitric acid, hydrochloric acid, *etc.* and manufacture of synthetic dyes, organic solvents, drugs, general medicines, explosives, plastics, *etc.*

Metals and their compounds are useful to mankind. Iron was the first trace elements shown to be essential in the human diet. It is a component of haemoglobin. Additional trace metals have been found to be essential to human nutrition : Cu, Mn, Zn, Co, Mo and Cr. Cobalt is a component of vitamin B₁₂. Both manganese and molybdenum are involved in formation of enzymes. Chromium is useful for glucose metabolism. Zinc is present in some of the enzymes and in the hormone insulin. Copper is involved in absorption and mobilization of iron required for haemoglobin. Metals form an important component of the mineral wealth of a country.

A few of the non-metals are hydrogen, oxygen, nitrogen, sulphur and phosphorus. The non-metals and their compounds play a vital role in chemistry and in our lives. Hydrogen and oxygen react with each other to form H₂O (water), a simple molecule, whose unusual properties are necessary for the development and maintenance of life. Sugar (or carbohydrates), an important source of energy, contains C, H and O. Proteins, the body building materials, contain C, H, O and N as their constituents. Detergents, vitamins, fertilizers, medicines, *etc.*, all contain some of the non-metals.

About 20 elements are found in the free state or the native state, whereas most other elements occur in the combined form. Now the question arises — which type of elements are found in the combined state and which elements in the free state?

Hydrogen, a typical non-metal is a very active element. The metals above hydrogen in the electrochemical series (Unit 10) are rarely found in the free state. The less active metals, that are below hydrogen in the activity series, often occur in the free state, *e.g.*, platinum and gold. Some metals, such as copper, silver and mercury are found both in the free and combined forms. Generally most electropositive metals occur in nature in association with the most electronegative non-metals, *e.g.*, halogens, oxygen, nitrogen (as NO₃⁻). Some other less electropositive metals, such as lead, copper, silver, zinc and mercury form stable and insoluble salts with sulphur.

Elements found in the combined form are often present as oxides, carbonates, sulphides, silicates, *etc.* Table 2.1 includes the metals which are associated with these forms in the nature. They have also been summarized in Fig. 2.1 in a manner which emphasises periodic relationship.

2.3 EARTH AS A SOURCE OF ELEMENTS

The earth is the source for all the substances directly available to us. Broadly there are three parts of the earth, each of which corresponds to one of the phases-solid, liquid or gas.

The crust or lithosphere is the solid part (siliceous shell) of the earth. More than 99% of the crust contains oxygen, silicon, aluminium, iron, calcium, sodium, potassium and magnesium and 75% is derived from the non-metals oxygen and silicon. About 80% of the earth's surface is covered with aqueous solution. This liquid layer (fresh and salt water) along with solid state water in continental snow and ice is called the hydrosphere. About 40 elements (Cl, Na, Mg, Br, K, *etc.*) are present in appreciable amounts in sea water. Surrounding the earth is the gaseous phase. This is called atmosphere. Nitrogen and oxygen are the major constituents of atmosphere.

TABLE 2.1 Distribution of elements

Mineral/Ore	Metals present
1. Native:	Cu, Ag, Pt, Hg, As, Sb and Bi
2. Oxide:	Cu (cuprite, Cu_2O), Fe (haematite, Fe_2O_3), Zn (zincite, ZnO), Al (bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$), Sn (cassiterite, SnO_2), Mn (pyrolusite, MnO_2), <i>etc.</i>
3. Sulphide:	Zn (zinc blende, ZnS), Hg (cinnabar, HgS), Cu (copper pyrites, CuFeS_2), Pb (galena, PbS), Ag (argentite, Ag_2S), Ni and As (nickel glance, NiAsS), Sb (stibnite, Sb_2S_3), As (mispickel, FeAsS), <i>etc.</i>
4. Carbonate:	Fe (siderite, FeCO_3), Zn (calamine, ZnCO_3), Cu (malachite, $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$), Ca and Mg (dolomite, $\text{MgCO}_3 \cdot \text{CaCO}_3$), Sr (strontianite, SrCO_3), Ca (limestone, CaCO_3), <i>etc.</i>
5. Sulphate:	Ba (barytes, BaSO_4), Ca (gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), Sr (celestine, SrSO_4), Pb (anglesite, PbSO_4), <i>etc.</i>
6. Silicate:	Be (beryl, $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$), Li (spodumene, $\text{LiAl}(\text{SiO}_3)_2$), Ni (garnierite, $\text{H}_2(\text{Mg}, \text{Ni})\text{SiO}_4$), Zn (willemitite, Zn_2SiO_4), Al (kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), <i>etc.</i>
7. Halide	Na (rock salt, NaCl), K and Mg (camallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), Al (cryolite, Na_3AlF_6), Ag (horn silver, AgCl), Ca (fluorspar, CaF_2).

Thus, most of the elements are found in the natural deposits in the earth's crust, oceans and atmosphere. These deposits are called minerals. Some of the metals, *e.g.*, magnesium is extracted from sea water (magnesium found in sea water was primarily dissolved from the rocks of the earth's crust). Thus, minerals are naturally occurring homogeneous inorganic substances of almost defined chemical composition. Small amounts of iron and iron-nickel alloy are found in meteorites (solids) which come

from outer space. In Table 2.2 the relative abundance of the common elements in earth's crust (rock) is summarized. The erratic variation of the abundance of the elements in the earth's crust is also portrayed through Fig. 2.2. It is clear from the Table 2.2 and Fig. 2.2 that many elements for which the demand is high do not occur in large amounts. Fortunately, however, their distribution is not uniform. Some of the elements are found in large amounts in several locations.

TABLE 2.2 Abundance of the elements

Elements	Earth's crust (mass%)	Some commonly occurring forms
Oxygen	46.6	Silica, silicates, metallic oxides
Silicon	25.8	Silica (sand, quartz, agate, flint) silicates (felspar, clay, mica)
Aluminium	7.5	Silicates (clay, felspar, mica), oxide (bauxite)
Iron	4.7	Oxides (haematite, magnetite)
Calcium	3.4	Carbonates (limestone, marble, chalk), sulphate (gypsum)
Sodium	2.6	Chloride (rock salt), silicates (felspar, zeolite)
Potassium	2.4	Chloride, silicates (felspar, mica)
Magnesium	1.9	Carbonate, chloride, sulphate
Hydrogen	0.7	Organic matter
Titanium	0.4	Oxide
Chlorine	0.2	Common salt (NaCl), sylvite (KCl), carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)
Phosphorus	0.1	Phosphate rock [$\text{Ca}_3(\text{PO}_4)_2$], organic matter
Manganese	0.09	Oxide (pyrolusite)
Carbon	0.08	Diamond, graphite, coal
Sulphur	0.06	Native, sulphides
Barium	0.04	Sulphate (barytes), carbonate (witherite)

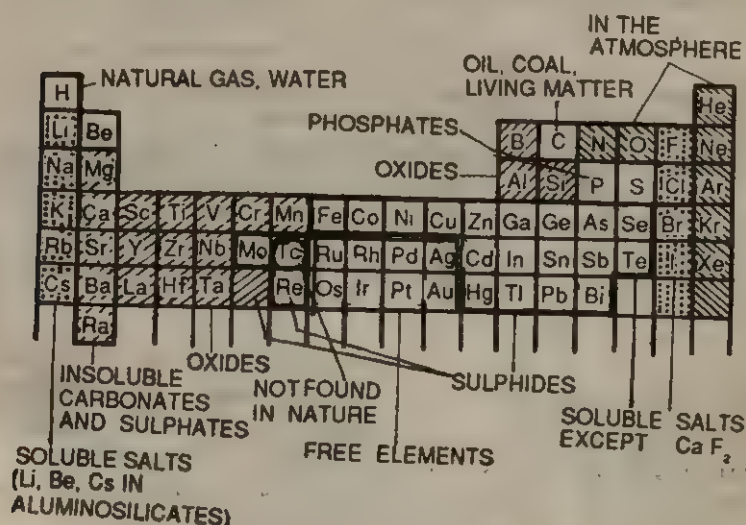


Fig. 2.1 Occurrence of the elements

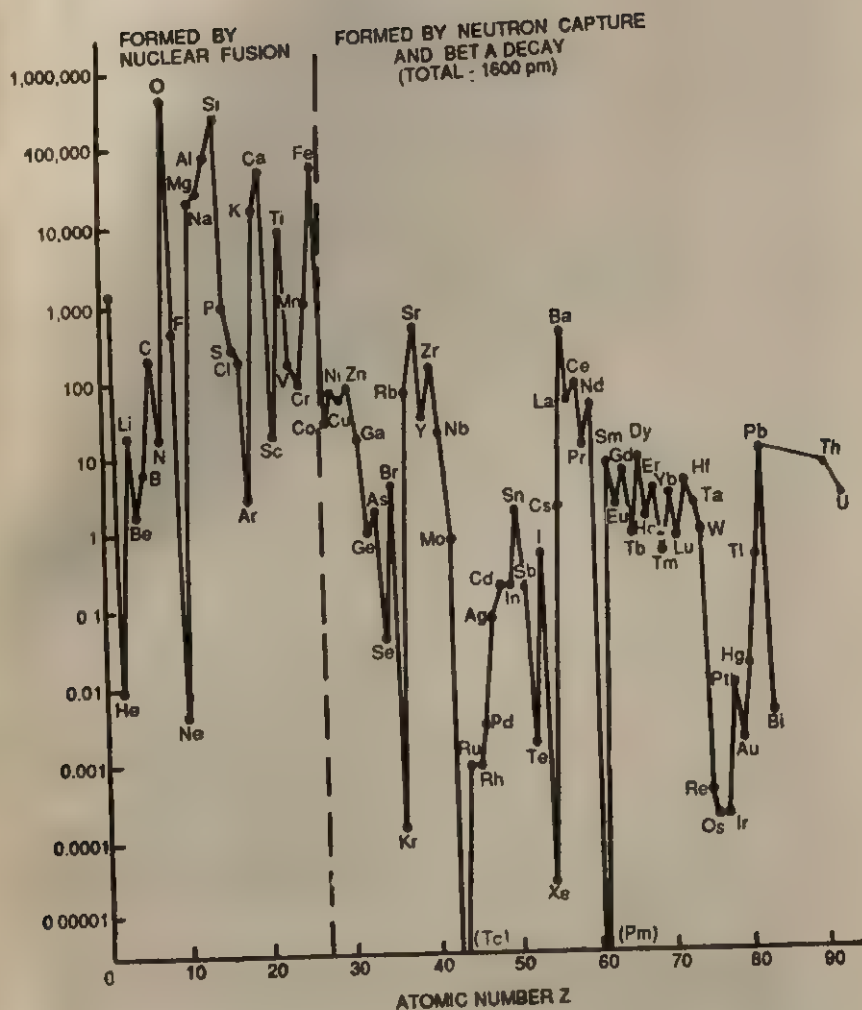


Fig. 2.2 Crustal elemental abundance as a function of atomic number

Our direct contact with the solid earth is limited to the crust, the thin skin averaging 10-50 km in thickness and making up less than one percent of the earth's total mass. The knowledge of the earth's interior has been collected and analyzed on the basis of indirect evidence collected from the study of the transmission of earthquake waves and thermal energy, the earth's magnetism, its gravity and other geophysical effects.

Rocks are the major portion of the earth's crust. These rocks are mostly siliceous matter. About 95% of the earth's crust consists of igne-

ous rocks. Rest of about 5% of the earth's crust has undergone physical, mechanical and chemical weathering processes, and thus, producing about 90% of the mineral sources. The rocks of the earth's crust are classed as igneous, metamorphic and sedimentary. The parent material of these rocks is 'magma' (rock mobile at high temperatures).

(i) **Igneous rocks** : In the cooling of the earth, the initial gaseous matter condensed to a liquid (molten matter). The molten matter (present well within the earth) is termed 'magma'. Magma is associated with considerable amounts of gases such as H_2O , HCl , CO_2 and H_2S . Pressure changes, within the body of the earth, make the molten matter move upward into the higher regions of the earth's crust. In this movement, a major part of the magma solidifies before reaching the surface of the earth and the remaining part erupts through cracks in the surface of the earth in the form of lava (lava on cooling forms basalt rock). Thus, rocks (solidified magma) below the surface are called 'Igneous rocks'. The chief products of these rocks are granite and basalt (contains quartz and ferromagnesium compounds). Minerals, such as feldspar, mica and magnetite are also associated with these rocks. Igneous rocks, generally formed in the absence of air, are chemically unstable at the earth's surface and react with water, oxygen and CO_2 forming new minerals.

(ii) **Sedimentary rocks** : These rocks are formed when the constituents of atmosphere and hydrosphere (frost, rain, water, etc.) react with earth's crust. This is called the weathering process. The solid products, e.g., oceans, lakes, rivers, etc., and deposit as sediments. This process continues for centuries together, until the sediments accumulate at some place and become firm under pressure and form sedimentary rocks. Some of these rocks are also formed from the organic materials (trees, etc.) accumulated under earth. These are made of layers and are also termed laminated or stratified rocks. Several of the chemical changes which occur in the weathering process of the earth's crust (igneous rock) are shown in Fig. 2.3.

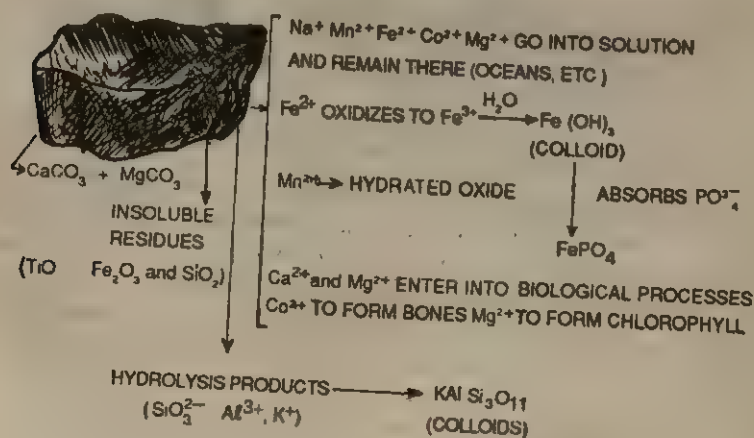


Fig. 2.3 Weathering of an igneous rock.

(iii) **Metamorphic rocks** : Effects of temperature and pressure convert igneous and sedimentary rocks into new types of rocks called metamorphic rocks. About 50% of the sedimentary rocks in the earth's crust is shale (slate), a rock formed by hardening of clay and other small particles of quartz, feldspar, *etc.* These shales have finely stratified-structures. Once formed, their composition remains unaltered under high pressures and temperatures. Marble is another example which has been formed from sedimentary rocks. Garnet, kyanite, sillimanite, *etc.*, also constitute these rocks.

The earth model that geologists use to explain the density (5.5 g/mL) suggests an inner core consisting of solid iron, although its temperature is very high, *i.e.*, 2273K. The solid state has probably been maintained by very high pressure, *i.e.*, greater than 3×10^6 atm prevailing in that region. Surrounding the inner core is an outer core which contains molten iron and small quantities of lighter elements such as silicon, sulphur, nickel, *etc.* This region is being surrounded by mantle. This is the largest part of the earth which accounts for 80 percent of the volume and 67 percent of the mass. This is mainly composed of magnesium and iron-rich silicate minerals.

According to V.M. Goldschmidt the earth consists of inner core covered by different layers to give it a characteristic shape. He also suggested that cooling of the gaseous matter resulted in major parting leading to segregation of different zones - a metallic core, an intermediate sulphide layer, covered by a silicate crust which in turn is enveloped by solid crust and finally by atmosphere (Fig. 2.4). The boundaries between the different regions of the earth's interior are not very sharp, nor is the situation static. Over many millions of years - there is a shifting and heaving of layers. In the process, crust is affected to a large extent. The shifting and heaving of layers cause the continents to drift and push up the mountains ranges.

The presence of the different layers and their geological conditions reveal the association of different materials with these layers. The composition of the materials in these layers at different places is also different. The distribution of elements in the inner core (siderophil), sulphide zone (chalcophil), silicate crust (lithophil) and the atmosphere (atmosph) is quite different. The distribution of elements in the different zones is given in Table 2.3. The presence of one particular element in different combined forms found in various parts of the solid phase of the earth explains the relative stabilities of the different materials. The presence of one element in more than one layer reflects its easy accessibilities.

Another view, about the composition of the earth, has been proposed by two Swiss scientists W.Kuhn and A.Rittmann. According to

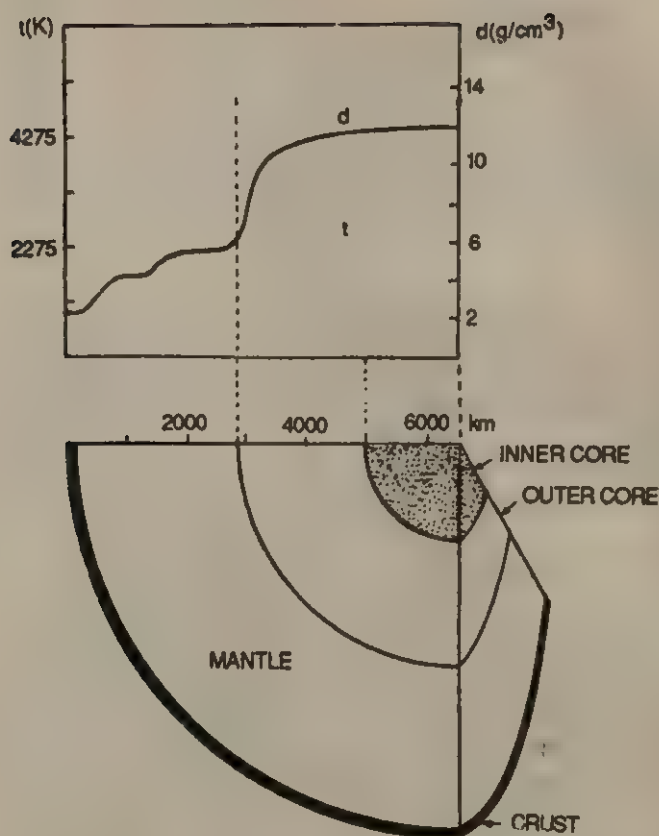


Fig. 2.4. Regions of earth suggested by Goldschmidt. The earth's crust is outer layer averaging 10-50 km in thickness

this the core of the earth constitutes solar material containing 30% hydrogen followed by molten silicates covered with magma layer and crust.

TABLE 2.3 Distribution of elements in different layers

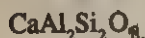
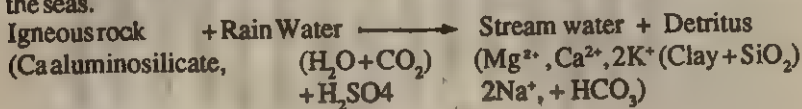
Layer	Composition
1. Siderophil (Innercore)	Fe, Mn, Co, Ni, Cu, Ru, Rh, Pd, Ag, Re, Os, Ir, Pt, Au
2. Chalcophil (Outer core)	P, S, Zn, Ga, Ge, As, Se, Cd, In, Sn, Sb, Te, Hg, Tl, Pb, Bi
3. Lithophil (Silicate crust)	Chlorides, sulphates and carbonates of Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Silicates and oxides of Be, Al, Si, Y, La, Ac, Ti, Zr, Hf, Th, V, Nb, Ta, Cr, Mo W, U F, Cl, Br, I, B, C, Si, N, O, He, Ne, Ar, Kr, Xe.
4. Atmosphill	

2.4 ELEMENTS IN BIOLOGY

The importance of the elements for living systems has already been emphasized in Section 2.2. The list can further be extended by including the enrichment of iodine in sea weeds, vanadium in sea cucumbers and potassium in plant life. Zinc is found in the eyes of certain animals and magnesium in chloroplast. The chloroplasts have also been found to have the traces of Fe, Mn and Cu. Plants have curious ability to remove certain materials from soil or water and to store them in their own tissues. The horse tail (equisetum) removes gold and silica from the soil, the locoweed takes up barium while certain weeds extract potassium and iodine from sea water. The association of a particular element with a particular biological function is yet to be cracked.

2.5 ELEMENTS IN SEAS

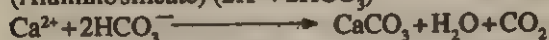
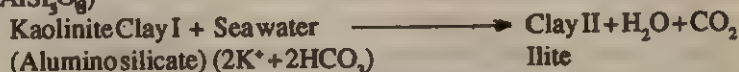
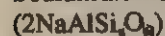
Products carried by the stream of water fall into sea. These products are continuously being obtained from the weathering of rocks. These can be understood from the following reactions taking place in the seas and outside the seas.



Potassium aluminosilicate,



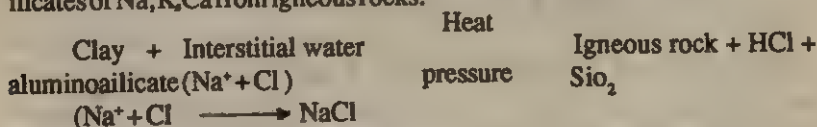
Sodium aluminosilicate,



This reaction has been possible by the curious ability of marine organisms to remove certain materials from water and to store them in their own tissues. Shells (CaCO_3) are formed. The calcium carbonate form sediments. Under sea, volcanoes evolve HCl which reacts with HCO_3^- .



and this reaction is followed by metamorphosis of clay forming aluminosilicates of Na, K, Ca from igneous rocks.



The relative abundance of the elements in sea water is shown in Fig. 2.5. Only a few elements, Cl, Br, I, Na, Mg, are recovered commercially from sea water.

2.5. OCEANS - THE GREAT STORE HOUSE OF CHEMICALS

The oceans that cover a large portion of earth's surface have been

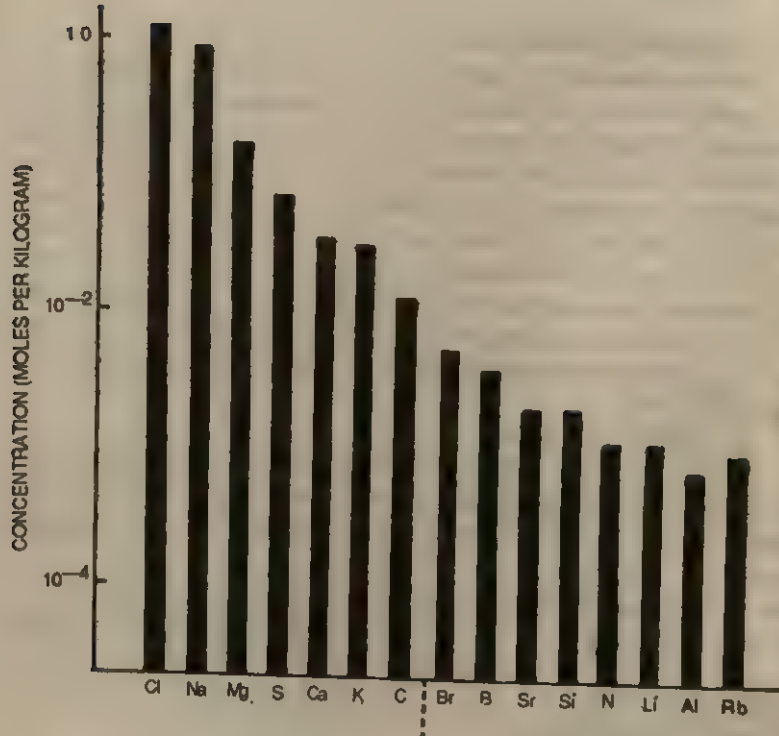


Fig. 2.5. The relative abundance of the elements in seawater.

termed "the world's greatest mine". Rivers and volcanic eruptions continuously keep adding minerals and metals to the mineral wealth of oceans. Part of this wealth in the ocean is present in dissolved state and some is lying as deposits onto the ocean floor. Sea water is a rich source of common salt, magnesium, sulphur, calcium, potassium, and bromine. Some other elements which are found in lesser quantities are, Sr, B, F, I, Fe, Cu, Pb, Zn, U, Ag, Au, Ra, and Ni. Our mineral deposits in the earth's crust are being depleted at an ever increasingly rapid rate. So it is necessary to look to the oceans for future supplies of the metals which have been harnessing our modern way of life.

The first mineral to be 'mined' from sea water was undoubtedly salt. Salt is a raw material for many chemical industries, especially the alkali and chlorine industries. Sea water is the leading source of bromine and magnesium. Processes are now in use by which these two elements are extracted from the sea water. Natural gas, oil, coal, sulphur, gold, and tin are amongst the important products extracted commercially from the seas. The sea-beds are richer in Ni, Cu and Zn than the sources available on the land. Sea weeds are the best source of iodine, alginic

acid, agar-agar and laminarin. Many other metals such as Au, Cu, Ag, K, and U can be extracted from sea water. But it is too expensive to extract these elements from the sea with our present techniques.

The ocean is a potential source of uranium. It is likely to be our chief energy fuel when our fossil fuels are exhausted. Pure water is obtained from sea water by 'flash distillation', a technique of distillation at low pressure. But it is too expensive. Countries, like Kuwait and Saudi Arabia, who are facing the scarcity of water are getting their supply from sea water. Desalination of sea water is likely to assume importance in near future. Presently, there are more than 2000 desalination plants all over the world which are equipped with the principle of flash distillation, ion exchange or reverse osmosis.

2.6 EXTRACTION OR METALLURGY OF METALS

Metallurgy is the art or science of separating metals from their ores and preparing them for use by smelting, refining or their other processing. Much of what is known about metallurgy was discovered centuries ago by hit and trial. Many of the early methods have been greatly improved and new methods have been discovered by scientific research.

Extraction of the elements from their naturally occurring ores is one of the world's major industrial activities. The form in which an element occurs in nature depends on its chemical properties, and therefore, is related to its place in the periodic table. The naturally occurring material in which the elements are present in stable compounds is called mineral. Those minerals from which metals are extracted profitably are called mineral ores or ores. Generally mineral ores are supposed to be present in abundance. Mineral ores may contain free metals or chemical compound of the metals.

Thus, all the ores are minerals but all minerals cannot be ores. A mineral, e.g., galena (PbS) is always galena, but a mineralized rock containing galena may or may not be a lead ore. Both bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) and clay ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) are minerals of aluminium. It is only bauxite which is generally employed for the commercial production of aluminium. Thus, bauxite is an ore and not clay of aluminium. Metals and their ores are usually associated with earthy materials such as rocks, clays and sand called matrix or gangue. For example, an ore of lead and zinc may contain the mineral galena (PbS) sphalerite (ZnS), pyrite (FeS), siderite (FeCO_3) and quartz (SiO_2). The galena and sphalerite are the ores and pyrite, siderite and quartz are the gangue or matrix. In Table 2.4 the minerals of some metals are listed. The minerals employed as ores are italicized.

TABLE 2.4 Metals and their minerals; minerals italicized are used as ores

Metal	Minerals with their chemical composition
1. Lithium, Li	<i>Spodumene</i> , $\text{LiAl}(\text{SiO}_3)_2$; <i>Petalite</i> , $\text{LiAl}(\text{Si}_2\text{O}_6)_2$
2. Sodium, Na	<i>Rock salt</i> , NaCl ; Chile saltpetre or Caliche, NaNO_3 ; <i>Borax</i> , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
3. Magnesium, Mg	<i>Magnesite</i> , MgCO_3 ; <i>Dolomite</i> , $\text{MgCO}_3 \cdot \text{Ca}(\text{CO}_3)_2$; <i>Carnallite</i> , $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$; <i>Olivine</i> , Mg_2SiO_4 ; <i>Epsomite</i> , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
4. Aluminium, Al	<i>Bauxite</i> , $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$; <i>Cryolite</i> , Na_3AlF_6
5. Potassium, K	<i>Sylvite</i> , KCl ; <i>Car salite</i> , $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; <i>Orthoclase</i> , $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$; Indian saltpetre, KNO_3
6. Calcium Ca	<i>Limestone</i> , iceland spar and marble, CaCO_3 ; <i>Dolomite</i> , $\text{CaCO}_3 \cdot \text{MgCO}_3$; <i>Gypsum</i> , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; <i>Fluorspar</i> , CaF_2
7. Titanium, Ti	<i>Rutile</i> , TiO_2 ; <i>Ilmenite</i> , $\text{FeO} \cdot \text{TiO}_2$
8. Chromium, Cr	<i>Chromite or chrome iron</i> , $\text{FeO} \cdot \text{Cr}_2\text{O}_3$; <i>Chromo ochre</i> , Cr_2O_3 ; <i>Crocoisite</i> , PbCrO_4
9. Manganese, Mn	<i>Pyrolusite</i> , MnO_2 ; <i>Braunite</i> , Mn_2O_3 ; <i>Manganite</i> , $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$; <i>Hausmanite</i> , Mn_3O_4
10. Iron, Fe	<i>Haematite</i> , Fe_2O_3 ; <i>Magnetite</i> , Fe_3O_4 ; <i>Siderite</i> , FeCO_3
11. Nickel, Ni	<i>Pentlandite</i> , $(\text{Ni}, \text{Cu}, \text{Fe})\text{S}$; <i>Kupfernickel</i> or <i>nicolite</i> , NiAs
12. Copper, Cu	<i>Copper glance</i> , Cu_2S ; <i>Copper pyrites</i> , CuFeS_2 ; <i>Cuprite</i> , Cu_2O ; <i>Malachite</i> , $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$
13. Zinc, Zn	<i>Zinc blende</i> , ZnS ; <i>Calamine</i> , ZnCO_3 ; <i>Zincite</i> , ZnO
14. Silver, Ag	<i>Horn silver or chlorargyrite</i> , AgCl ; <i>Argentite or Silver glance</i> , Ag_2S ; <i>Pyrargyrite</i> or <i>ruby silver ore</i> , Ag_3SbS_3 ; <i>Native silver</i>
15. Tin, Sn	<i>Tinstone or Cassiterite</i> , SnO_2
16. Antimony, Sb	<i>Stibnite</i> , Sb_2S_3
17. Mercury, Hg	<i>Cinnabar</i> , HgS
18. Lead, Pb	<i>Galena</i> , PbS
19. Gold, Au	<i>Native gold</i>
20. Bismuth, Bi	<i>Bismuth glance</i> , Bi_2S_3 ; <i>Bismite</i> , Bi_2O_3 ; <i>Bismuthite</i> , $(\text{BiO})_2\text{CO}_3$

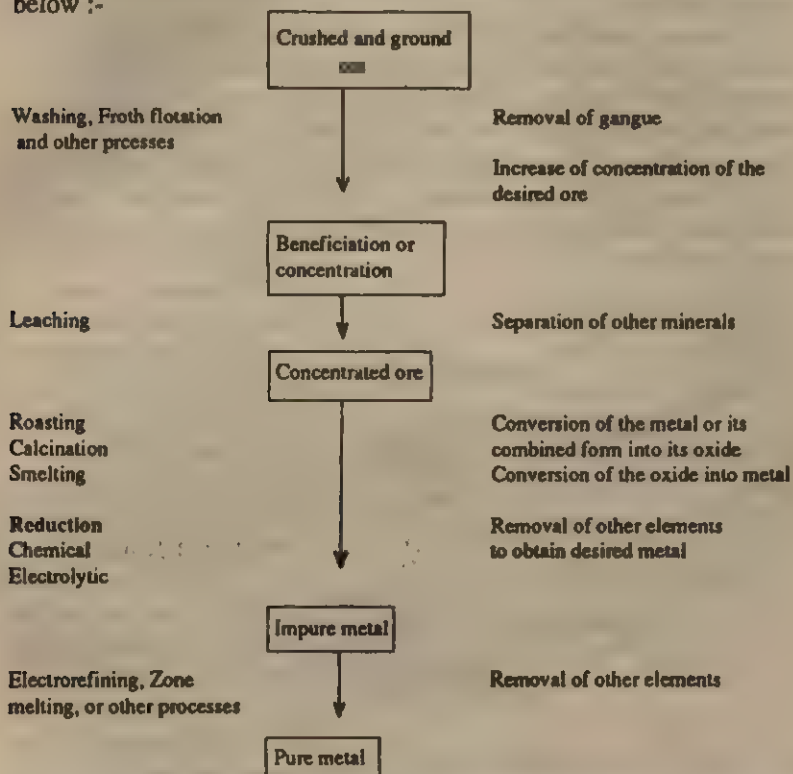
2.6.1 Metallurgical Processes

To extract the metals from ores, several physical as well as chemical processes are employed. The choice of the process depends upon the nature of the ore and the local conditions.

The extraction of all metals from their naturally occurring ores involves three stages.

- (i) Purification (separation from gangue), and concentration (or beneficiation or dressing of the ore) of the ores; its conversion into some form suitable for subsequent processes
- (ii) Conversion of the enriched ore into metal
- (iii) Purification (refining) of the metal

The various stages involved in the extraction of metals starting from the concentration of ore to the present form of metal are outlined below :-



In the flow diagram above, the functions of different processes are given on the right side. On the left side, the various methods that are used are denoted. There are also other methods that are not listed here.

2.6.2 Production of Concentrated Ore

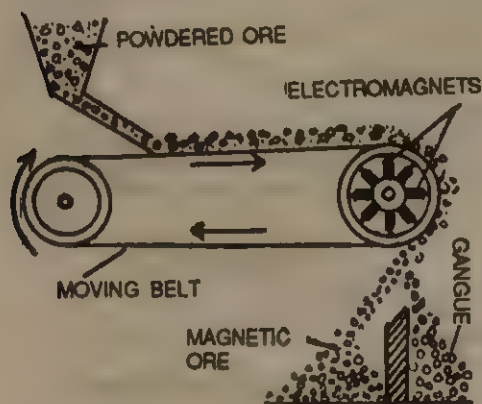
In mining operations, the desired mineral from which a metal is to

be extracted often remains associated with some rocky material as impurities. The percentage of the desired metal is very small. Thus, it is necessary to separate the ore from the gangue before proceeding with other metallurgical operations. Undesired material can be removed either by physical or chemical methods or a combination of both.

Physical methods include gravity separation and flotation processes. In some cases, where the ore contains a magnetic constituent, this characteristic can be employed in the concentration. **Chemical methods** are those of hydrometallurgy. This is the leaching of ores by aqueous solution to extract the desired metal in the form of one of its soluble salts.

Physical methods

Ores are generally found mixed with varying amounts of dirt, rock sand and other impurities. Several steps are usually necessary to remove this **sludge**, as it is called. Sometimes gross lumps of sludge are removed by hand (Pickling). The first stage consists of grading, pulverizing and grinding of the ore into small pieces in crushers and grinders. This is followed by the concentration of the metal bearing parts. The nature of the process used for concentration depends upon the nature of impurities and ore.



Magnetic material can be separated from non-magnetic impurities by using strong electromagnets (Fig. 2.6). This technique is used in the separation of magnetic chromite (an ore of chromium), magnetite (Fe_3O_4) or pyrolusite (MnO_2) from the gangue particles. A magnetic ore (wolframite, FeWO_4) can also be separated from the non-magnetic ore (cassiterite, SnO_2) by this method.

Fig 2.6 Magnetic concentration of ore.

In some other cases, differences in the density between the ore and its impurities may be advantageous for the separation of crushed material on an agitated **sloping table** (Fig. 2.7). The heavier ore particles collect behind the wooden strips. The lighter gangue particles are washed away in a stream of water. The gravity separation can also be done in a **hydraulic classifier** (Fig. 2.8).

In this, a strong stream of water is pumped through the bottom. The lighter gangue particles are carried away by the upward thrust of

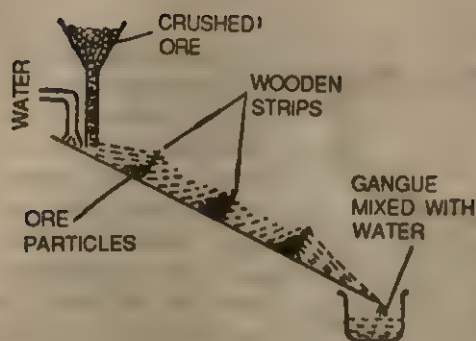


Fig. 2.7 Separation of gangue particles from ore particles using the sloping table (The Wifley table)

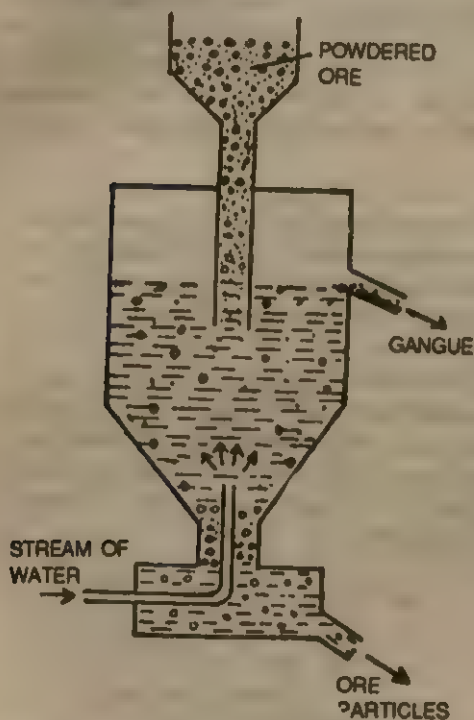


Fig. 2.8 Separation of gangue particles from ore particles using the hydraulic classifier.

water leaving behind the heavier ore particles at the conical base. This operation is designated as levigation. The ores of tin and lead ore concentrated by this method.

Another method usually used for purifying the sulphide ores is froth flotation (Fig. 2.9). In this, the powdered ore is added to water containing pine oil (frothing agent) and sodium ethyl xanthate (collecting agent). Here, the separation is possible because of the different densities of the materials and their preferential wetting characteristics with the frothing agent and water. A vigorous stream of air is now passed through the mixture which thoroughly agitates it and disperses the oil into colloid sized particles. As a result, the metal particles (but not the sludge particles) stick to the oil droplets and rise to the surface in the form of froth supported by air bubbles. Water wets the gangue particles which sink to the bottom. This technique is useful for concentrating dense ores such as galena and zinc

blende. With this method, it is also possible to separate one ore from another.

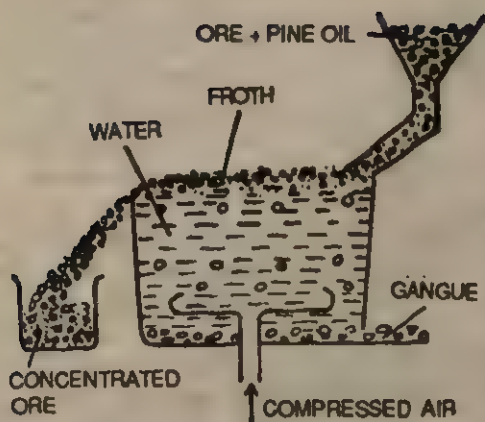


Fig. 2.9 Concentration of the sulphide ores by the froth flotation process.

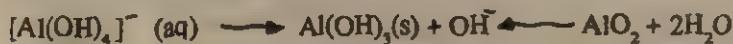
The separation can also be achieved by taking the advantage of the difference in melting points of metal bearing portions and impurities. Ores having melting points lower than that of impurities are heated on the sloping floor of a furnace (Fig. 2.12) to a temperature just above the melting point of the metal. The liquid metal is drained away from the gangue. This method is

called liquation. Stibnite (Sb_2S_3) is concentrated by this liquation method. The native ores of silver, gold, etc., are concentrated by amalgamation.

Chemical Methods

Chemical properties of minerals make the basis of these methods.

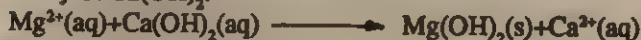
Leaching : In this process, the powdered ore is dissolved selectively by using an appropriate acid, base or other reagents. It reacts only with ore. By this method the aluminium ore is concentrated. Bauxite, an ore of aluminium, contains hydrated oxides of Al, and Fe, silica, clay and TiO_2 . The ore is treated with hot sodium hydroxide solution. Because of the amphoteric nature of the aluminium ion (aluminium oxide is amphoteric - soluble both in strong acids and strong bases) the alumina is dissolved away as aluminates from the ore impurities while iron (Fe_2O_3 , a basic metallic oxide, insoluble in strong bases) and other impurities remain undissolved and are filtered off.



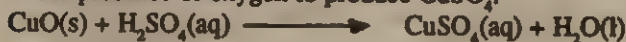
This method of purification is known as Baeyer's process.

Some Important Examples of Leaching

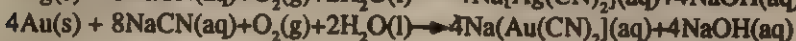
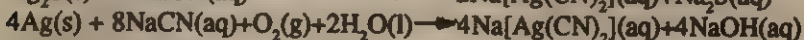
1. Mg^{2+} ions present in sea water are precipitated as hydroxide with a slurry of $\text{Ca}(\text{OH})_2$.



2. The low grade carbonate and oxide ores of copper are leached with dilute H_2SO_4 . Sulphide ores of copper are also treated with H_2SO_4 in the presence of oxygen to produce CuSO_4 .



3. The leaching of silver ores (sulphide or native) and native gold is carried out with sodium cyanide solution to produce stable complex ions with the cyanide ion.



The presence of oxygen is necessary to convert gold to the oxidized state.

4. Sulphide ore containing Ni, Co and Cu is leached with aqueous ammonia under oxidizing conditions to form the metal ammine complexes. Some specific bacterial systems are known to remove preferentially some metals from the ores. These can be used to separate metals selectively in low concentration (Section 2.4).

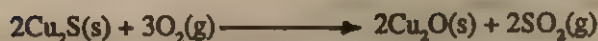
Calcination and Roasting

Volatile impurities may be removed by heating the ore strongly in the absence of air (calcination). On calcination, carbonates, hydroxides, oxides, *etc.*, lose moisture, carbon dioxide and other volatile impurities.



Most sulphide ores are generally heated in a stream of air (roasting) to convert them to oxides and to remove sulphur as sulphur dioxide.





Sometimes oxidation is effected directly to the sulphate, *e.g.*, galena is converted to lead sulphate. Some roasting reactions are given below :



2.6.3 Production of the Metals

The concentrated ore is either directly converted to a metal or to a compound which is suitable for reducing to the metal. This step depends upon the nature of impurities present and the metal bearing ore.

(I) Wet Chemical Processes

Leaching (treating the ore with some chemical substances) and **metal displacement technique** are the two wet processes.

1. **Leaching** : This process has already been discussed under the concentration of the ores. This is also a method of purification.

Copper sulphate, aluminium hydroxide and magnesium hydroxide obtained on leaching the ores can be used as such or converted to free metals.

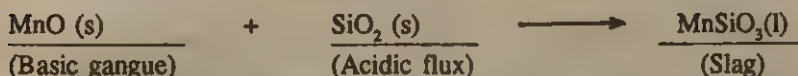
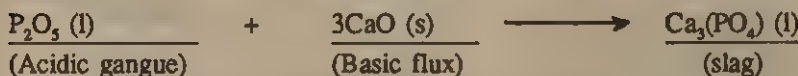
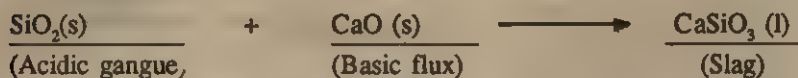
2. **Metal displacement method** : Ores of silver and gold on leaching with cyanide solution give soluble complex salts. By adding zinc, both silver and gold can be precipitated from the aqueous solution. A soluble cyanide complex of zinc is produced.



II. Dry Chemical Processes

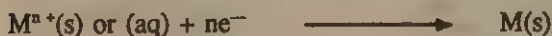
Metals in the middle of the activity series (such as zinc, iron, lead and copper) can be extracted from their oxides and sulphides in the fused state by using some reducing agents. Very often the sulphides are converted to oxides before reduction to the metal. This process of reduction is called **smelting**.

Concentrated ores still contain some gangue at this stage and this is separated by adding **flux**. Flux is a compound which reacts with the gangue forming a compound which melts at low temperature. This compound is called **slag** (easily fusible). Flux materials are used depending upon the acidic and basic character of oxides. Thus, reduction and slagging take place simultaneously. For the removal of acidic gangue (sand) a basic flux of limestone is added to form a fusible slag of calcium silicate (molten at the reduction temperature). The molten slag is easily removed from the used metal because of the difference in their densities. They are also insoluble in each other.



The removal of impurities from concentrated ore by forming molten slag is called **slagging operation**. The slag consists of the molten impurities generally as metal silicate.

The preferred method of reduction of an ore to the free metal is decided mainly by the relative ease of achieving the reaction.



Some methods used for reduction of ores are listed in Table 2.5 and summarized in Fig. 2.10.

The basis of smelting (chemical reduction) is to remove oxygen of the metal oxides by treating them with carbon, carbon monoxide or another element for which oxygen has a stronger affinity and forms a more stable oxide. The electrons also serve as reducing agents to reduce metallic oxides to metals (electrolytic reduction). Molten oxides and halides are used in this type of reduction. The choice between the chemical and electrolytic reductions depends upon redox potentials. Metals with large negative

potentials cannot be obtained from their ores by the chemical reduction method. Some metal oxides such as Al_2O_3 are resistant towards chemical reducing agents; hence, the electrolytic method (Unit 14) is used.

The methods fall into four main groups.

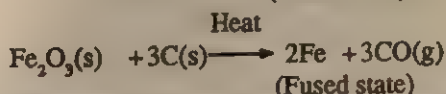
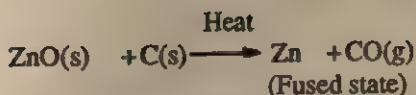
1. Reduction with carbon (also CO) or hydrogen.
 2. Thermal decomposition of an ore, without using any chemical reducing agent.
 3. Reduction by a reactive metal (e.g., Al or Mg)
 4. Electrolytic reduction of a molten oxide or salt.
1. Reduction of the oxide by carbon : The calcined or roasted ore is heated with coke (or carbon) in a closed furnace (Unit 15)

TABLE 2.5. Extraction of some elements

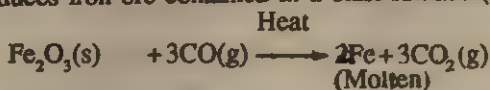
Element	E° (n)	Chief source	Extraction
K	- 2.92 (+ 1)	KCl: $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	Electrolysis of fused salts mixed with flux
Na	- 2.71 (+ 1)	NaCl	
Ca	- 2.87 (+ 2)	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; CaCO_3 ; CaCl_2	
Mg	- 2.36 (+ 2)	MgCl_2 ; $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	Electrolysis of Al_2O_3 in Na_3AlF_6 (Cryolite)
Al	- 1.66 (+ 3)	Al_2O_3	
Mn	- 1.18 (+ 2)	MnO_2	
Cr	- 0.74 (+ 3)	FeO , Cr_2O_3	(Thermite process)
Zn	- 0.76 (+ 2)	ZnS ; ZnO	
Fe	- 0.44 (+ 2)	Fe_2O_3	
Co	- 0.28 (+ 2)	CoAsS ; Co_3S_4	Chemical reduction with carbon (or hydrogen) of oxides. First convert sulphides to oxides by roasting.
Ni	- 0.25 (+ 2)	Sulphides	
Sn	- 0.14 (+ 2)	SnO_2	
Pb	- 0.13 (+ 2)	PbS	
Cu	+ 0.34 (+ 2)	CuFeS_2 ; Cu_2S	
Hg	+ 0.85 (+ 2)	HgS	Cyanide extraction (Leaching)
Ag	+ 0.80 (+ 1)	Metal; Ag_2S ; AgCl	
Au	+ 1.7	Metal, tellurides	
Cl	+ 1.36 (- 1)	NaCl	Electrolysis
F	+ 2.87	KHF_2	

E° , for reaction $\text{M}^{n+} + n\text{e}^- \rightarrow \text{M}$ (n given in parenthesis).

E° = Standard reduction potential at 298K



- (ii.) **Reduction of the oxides by carbon monoxide** : Carbon monoxide reduces iron ore contained in a blast furnace (Unit 15).



2. **Thermal decomposition of sulphide ores** : This method is used to obtain copper from sulphide ore (Unit 15). A part of the sulphide ore is first converted to oxide by roasting in air.

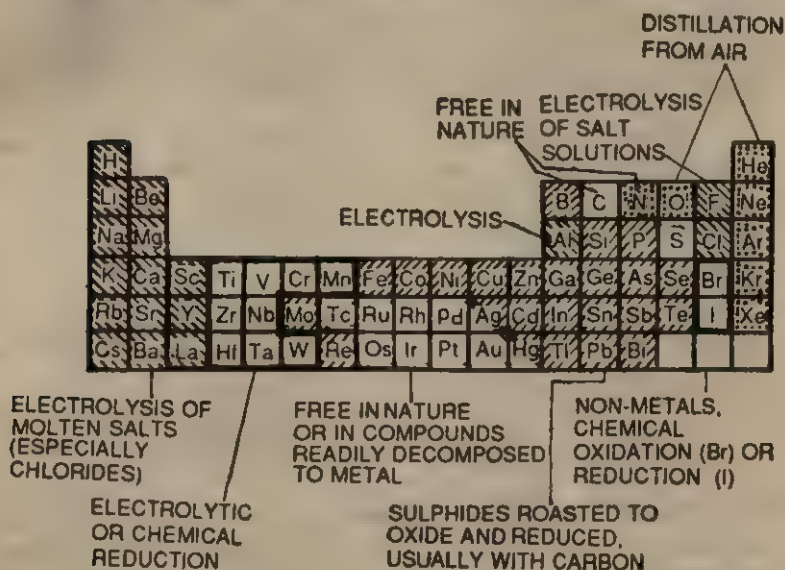
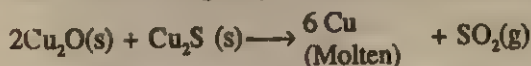


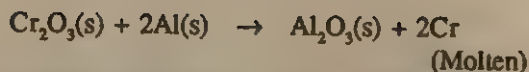
Fig. 2.10 Extraction of the elements



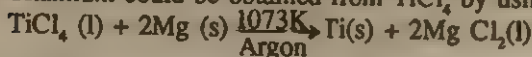
Now the heating is done in the absence of air. The remaining sulphide ore reacts with oxide giving the metal and sulphur dioxide.



3. **Reduction by a reactive metal (Aluminothermite process)** : Oxides of certain metals, which are not reduced by coke, e.g., are reduced using aluminium powder (Unit 15).



Titanium could be obtained from TiCl_4 by using magnesium metal.

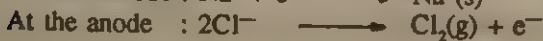
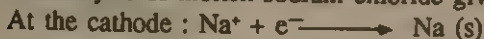


TiCl_4 is obtained by converting rutile (TiO_2) to liquid TiCl_4 .

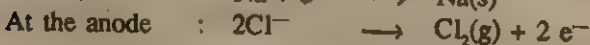
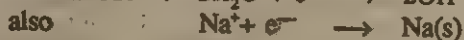
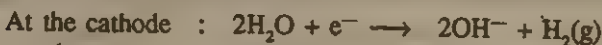
4. **Electrolytic reduction:** This method is used to extract potassium, sodium, calcium, magnesium, and aluminium from their fused compounds (usually chlorides; Unit 14). Chemical reduction of the oxides of these metals by coke (or carbon monoxide) is not practical as the temperature required for reduction is too high. Also, these metals cannot be extracted by electrolysis of their aqueous solutions since water present in the solution would be discharged at the cathode in preference to the metal ions.

The fused salts are subjected to electrolysis in specially designed cells (Unit 14). The electrodes used in cells are usually inert.

Electrolysis of molten sodium chloride gives,



The temperature necessary to produce molten NaCl is lowered by adding anhydrous calcium chloride. Electrolysis of aqueous sodium chloride gives.



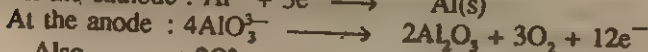
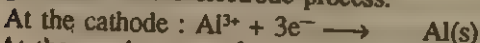
Aluminium is obtained industrially by the electrolysis of molten aluminium oxide in Hall's cell (Unit 14) at 1200K. Since the melting temperature of Al_2O_3 (2325K) is so high that electrolysis of the molten oxide cannot be accomplished, pure Al_2O_3 is dissolved in molten cryolite which has much lower melting temperature than oxide. Calcium fluoride is also added to lower the temperature of the melt.

It is postulated that the equilibrium

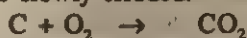


(Fused)

gives rise to the electrode process.

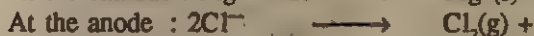
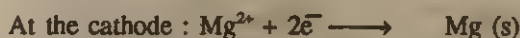


A part of oxygen escapes and the rest of it oxidizes the carbon anodes, which are slowly eroded.



The aluminium obtained is of 99.5% purity. If necessary, it can further be purified by electrolytic refining process.

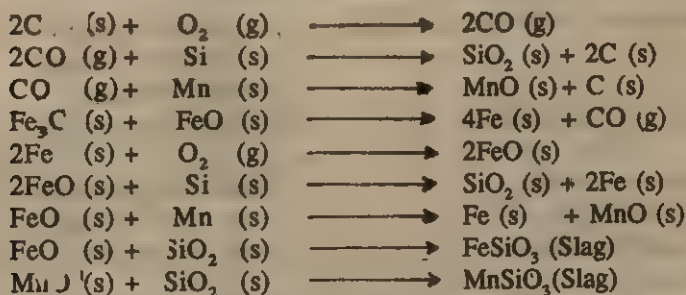
Magnesium chloride is melted and subjected to electrolysis to give magnesium metal.



2.6.4 Purification of the Metals

The metals obtained by the reduction of concentrated ores are associated with small amounts of unchanged ore, small amounts of other metals present in the ore, non-metals from the anionic part of the ore and some other impurities. For example, pig iron obtained from the blast furnace contains carbon, silicon, phosphorus, sulphur and manganese. The impurities are converted into their oxides and removed (oxidative refining). Generally, this method is employed when impurities can be oxidized more readily than the metal.

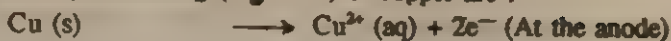
This is carried out in specially designed apparatus called Bessemer converter. Some of the reactions involved in the process are as follows :



Electrolytic refining. is another method which is widely used for purification purposes; Cu, Al, Ag, Pb, Co, etc. are electrolytically refined. A large block of impure metal from the reducing furnaces immersed in its salt solution serves as the anode. A thin sheet of pure metal is used as cathode. On passing current, the impure metal goes into solution as metallic ions and equal number of metallic ions are discharged and deposited as pure metal on the cathode. The impurities either are left as anode mud (or sludge) or remain in solution.

For blister copper (impure copper) copper sulphate is used as the electrolyte. Impurities usually associated with copper are iron, zinc, sulphur and some other metals in traces. The electrode processes which take place

in electrolytic refining (Fig. 2.11) of copper are :



Electrolytic refining of copper involves the principle of metal displacement reactions.

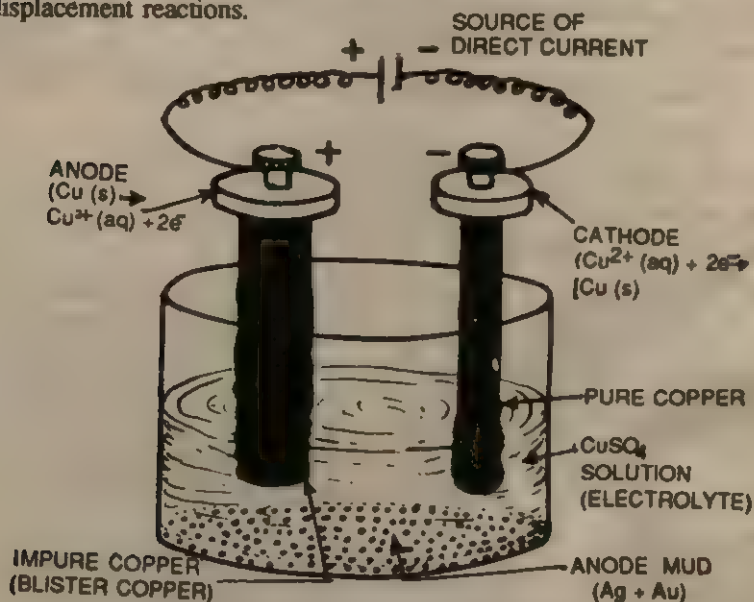
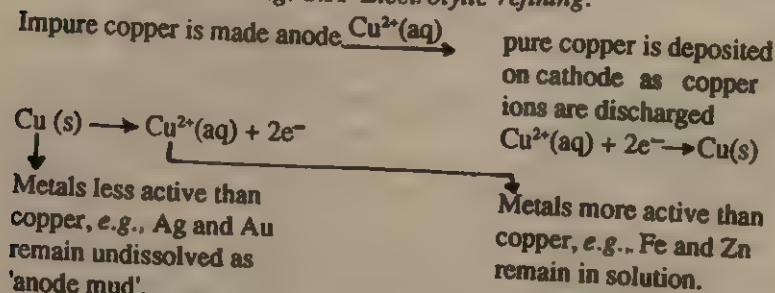


Fig. 2.11 Electrolytic refining.



Apart from these, there are a few more methods which are physical in nature. Volatile metals like mercury, zinc and cadmium are purified by distillation or sublimation. On heating, the volatile metals with low boiling points distill over leaving the less volatile impurities behind.

There is another method called liquation. In this method, impure metals are generally heated just above the melting points of the metals in a sloping hearth (Fig. 2.12). A low melting metal flows down leaving behind melting impurities. Readily fusible metals - Sn, Pb, Si, etc., are refined by this method.

Zone refining method is employed to prepare metals in an extremely high purity state, particularly germanium, silicon, boron and gallium for

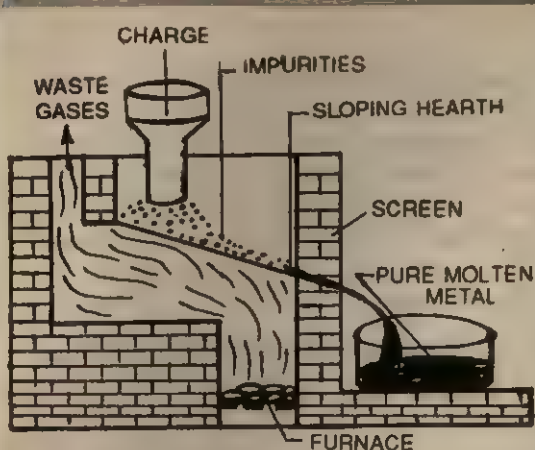


Fig.2.12 Liquation method for purification of metals

An impure rod of the metal is melted at one end with a circular heater (Fig. 2.13). The heater is slowly moved down the rod. With the slow shifting of the heater pure metal crystallizes out of the metal and impurities pass into the adjacent molten band (zone). Thus, the melted band is moved very slowly along the length of the rod, carrying the impurities with it. The process can be repeated a number of times. Each time the purity is increased. Finally, the end of the rod where the impurities have concentrated is discarded.

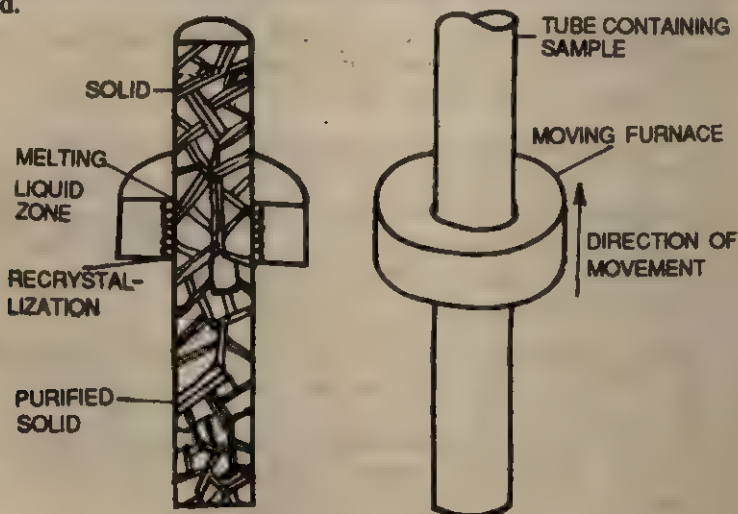


Fig. 2.13 Zone refining.

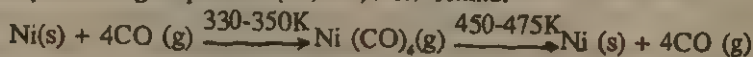
the manufacture of semiconductors and transistors. This involves the removal of impurities by fractional crystallization. This technique is used for the removal of impurities which show a difference in their solubility in the molten and solid states of a matter with which they are associated. Generally the impurities are more soluble in the metal than in the solid and concentrate in the metal.

Vacuum arc furnace refining method was developed for the refining of refractory metals. In the purification of such metals, sufficiently high temperatures are required to melt the impure metals. At the same time, chem-

ical reactions involving the metals at high temperature are also prevented. Crude metal, moulded into an electrode, is progressively melted in an arc furnace under vacuum. Volatile impurities vapourize off. Purified molten metal is transferred to precooled copper crucibles. Titanium, zirconium and molybdenum are purified by this newer technique. Further improvement has been made in this field. Energized electrons ejected from a heated tungsten filament are used to melt the metal. The metal (target) is bombarded with electrons under high vacuum.

Van Arkel method involves the thermal decomposition of a metal compound. This is employed for the purification of titanium, hafnium, zirconium, silicon, beryllium, *etc.*

Transition metals form volatile carbonyl with carbon monoxide, *e.g.*, $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$, *etc.* In the **Mond's process** impure nickel (spongy nickel) is heated with CO at 330 to 350K. Nickel produces nickel carbonyl, leaving impurities (Fe, Co, *etc.*) behind.



Pure nickel is obtained by heating the vapour of $\text{Ni}(\text{CO})_4$ to 450-475K when it decomposes to give powdered nickel.

A few less significant methods used for purification include, **cupellation**, **Parke's process** (distribution) and **poling**.

In Table 2.6, impurities associated with various metals and methods employed for their removal are summarized.

2.7 MINERAL WEALTH OF INDIA

1. India is on the world map on the basis of its mineral wealth. Bihar and Orissa have huge deposits of minerals of iron, manganese, copper and chromium. Bihar alone has huge deposits of coal, and mica. Both coal and mica deposits are available in Orissa also. In both the states, phosphates are also available. Singhbhum (Bihar) is very well known for its copper deposits.
2. Karnataka is well known for its Kolar gold mines. Apart from gold, minerals of iron and chromium are found in abundance.
3. Madhya Pradesh too has enough reserves of iron and manganese ores. Deposits of limestone, bauxite and coal are also available in enormous quantity.
4. Rajasthan is well known for its Khetri copper mines. The state is very rich in the minerals of non-ferrous metals like copper, lead and zinc. Mica and the mineral of beryllium are also available.
5. Tamil Nadu has huge deposits of iron and manganese ores. Magnesite (mineral of Mg), mica, limestone and lignite (a variety of coal) deposits are also found in abundance.

TABLE 2.6 Impurities associated with metals and their removal

Metal	Impurities	Method of refining
Aluminium	Copper, iron, silicon aluminium oxide, <i>etc.</i>	Electrolytic refining (Hoop's process)
Titanium	Iron, <i>etc.</i>	Electrolytic refining
Chromium	Iron, <i>etc.</i>	Electrolytic refining
Manganese	Iron, <i>etc.</i>	Electrolytic refining
Iron	Carbon, silicon, phosphorus, manganese and sulphur	Oxidative refining: oxides formed are removed as slag
Nickel	Cobalt, copper, iron platinum and other noble metals	Electrolytic refining
Cobalt	Nickel, copper and iron	Electrolytic refining
Copper	(a) Cuprous oxide (b) Iron, silver, gold, zinc and platinum metals	Poling Electrolytic refining
Zinc:		
1. Extracted by smelting	Cadmium, iron, lead and arsenic	Distillation
2. Extracted by electrolytic reduction of $ZnSO_4$	Iron, lead, copper, cadmium, arsenic, <i>etc.</i> , are removed before extraction	No further refining is required. Zn obtained is of 99.9% purity.
Silver	Lead	Parke's process (distribution) and cupellation
Cadmium	Zinc	Fractional distillation
Tin	Iron, arsenic, tungsten and sulphur	(1) Liquation followed by poling (2) Electrolytic refining
Gold	Silver, copper, zinc, lead, <i>etc.</i>	1. Cupellation to remove only lead 2. By dissolving impurities in H_2SO_4 or HNO_3 3. Electrolytic refining
Mercury	Zinc, lead, copper, tin, bismuth, <i>etc.</i>	Distillation in the presence of oxygen followed by treatment with 5% HNO_3 to dissolve impurities as nitrates. It may further be purified by vacuum distillation.
Lead	Silver, copper, iron, tin, antimony, bismuth, <i>etc.</i>	Oxidative refining followed by Parke's process or electrolytic refining.

In India, at BALCO (Bharat Aluminium Company Ltd.) and in other industries bauxite is the chief source of aluminium.

Zinc is mined chiefly as zinc blende from Zawar mines located near Udaipur in Rajasthan.

Iron deposits are found in West Bengal too apart from Bihar and Karnataka. Asansol, Durgapur, Jamshedpur, Bhilai, Bokaro, Rourkela and Bhadravati are the main iron producing centres.

2.8 QUALITATIVE TESTS OF METALS

A substance is analyzed to establish its qualitative or quantitative chemical composition. An analysis that yields informations only as to the identity of ingredients is known as qualitative analysis. Qualitative analysis of inorganic substances is primarily concerned with the detection and identification of the ions present in salts or mixture of salts. The salts, on dissolution in water, splits into positively charged ions called cations and negatively charged ions called anions. The cation is also known as basic radical and the anion as acid radical.

The detection and identification of metals are important in the metal extraction and purification processes. The extraction and purification of metals involve a variety of chemical reactions.

In qualitative analysis, various characteristic features of the chemical substances being analyzed are used for establishing its chemical composition. For example, ammonia gas can easily be identified by its distinct smell and ammonium salts by the liberation of ammonia gas when the salts are heated with caustic soda.

The physical properties of a salt, viz., colour, appearance, odour, etc. help in arriving at an inference regarding the salts as given in Table 2.7.

Table 2.7 Physical properties of salts

Physical property	Inference
White colour	Pb^{2+} , Al^{3+} , Zn^{2+} , Ca^{2+} , Ba^{2+} , Sn^{2+} , Mg^{2+} or NH_4^+ salts
Bluish or bluish green colour	Cu^{2+} or Ni^{2+} salts
Green colour	Cr^{3+} salts
Light green colour	Fe^{2+} or Ni^{2+} salts
Yellowish brown colour	Fe^{3+} salt
Light pink	Mn^{2+} salt
Pink or dark pink	Co^{2+} salt
Smell of ammonia gas	NH_4 salt
Smell of hydrogen sulphide gas	S^{2-} salt
Smell of sulphur dioxide gas	SO_3^{2-} salts
Deliquescent nature	Cl^- or NO_3^- salt

Further the colour of a salt indicates its constituents, e.g., copper carbonate is green, copper sulphide is black, cadmium sulphide is yellow, ferric hydroxide is brown and manganese sulphate is pink.

A substance on heating may sublime, decompose with evolution of gas or undergo certain other changes. Careful observation of the some conclusion (Table 2.8).

Some salts can be identified by the colour which they impart on heating to the colourless flame of bunsen burner. Flame test can be done by taking wet salt (made wet with conc. HCl) or by taking a dry salt. Sodium compounds turn the flame yellow; potassium salts violet; calcium salts brick red; barium and copper salts green and so on.

TABLE 2.8 Action of heat on salts

Observation	Inference and chemistry
1. Ammonium evolves, detected by smell.	Ammonium salts decompose on heating to give ammonia, $(\text{NH}_4)_2\text{CO}_3 \rightarrow 2\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}$
2. Carbon dioxide evolves, detected by allowing the gas to pass through lime water; Lime water turns milky.	Carbonates decompose on heating to give carbon dioxide, $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$
3. Sulphur dioxide evolves, detected by a filter paper soaked in $\text{K}_2\text{Cr}_2\text{O}_7$ solution; paper turns green.	Some sulphites and sulphates decompose to give sulphur dioxide $2\text{CuSO}_4 \rightarrow 2\text{CuO} + 2\text{SO}_2 + \text{O}_2$ $\text{Na}_2\text{SO}_3 \rightarrow \text{Na}_2\text{O} + \text{SO}_2$
4. Nitrogen dioxide gas evolves, detected by its colour and irritating smell.	Nitrates decompose to give NO_2 $2\text{Cu}(\text{NO}_3)_2 \rightarrow 2\text{CuO} + 4\text{NO}_2 + \text{O}_2$

Further to identify a salt, other substances (solids, solutions, *etc.*) called reagents are added to it. These reagents cause chemical transformations accompanied with the formation of new compounds possessing specific properties: a definite physical state (precipitate, liquid, gas); solubility in water, acids, alkalis and other solvents; a characteristic colour, odour and so forth.

The solubility of metal compounds in water, hydrochloric acid or an oxidizing acid is an important aspect of qualitative analysis. All cations have been divided into six analytical groups on the basis of the difference in solubilities of their chlorides, sulphides, hydroxides, carbonates under different conditions of acidity and alkalinity. The reagent used to precipitate the specific group is known as a group reagent.

TABLE 2.9 Solubility in water of some salts

Salt	Metals forming soluble compounds	Metals forming Insoluble compounds
Nitrates	Almost all the metals	
Chlorides	Most of the metals	Ag^+ , Pb^{2+} , Hg^+
Sulphides	Na^+ , K^+	Mg^{2+} , Ca^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , and almost all other metals depending upon the acidic and alkaline solution.
Hydroxides	Alkali and alkaline earth metals	Almost all the remaining metals
Carbonates	Na^+ , K^+	Ba^{2+} , Sr^{2+} , Pb^{2+} , Ca^{2+} , Ag^+ and many other metals
Sulphates	Very large number of metals	Ba^{2+} , Pb^{2+} , Ca^{2+} , Sr^{2+} , Ag^+
Oxides	Na^+ , K^+ , Ba^{2+}	Most of the other metals

Some metal oxides such as Al_2O_3 , SiO_2 , Cr_2O_3 and some salts, e.g., BaSO_4 , AgCl , PbSO_4 , etc., are quite inert. In these cases, one has to heat them for long with fusion mixture ($\text{Na}_2\text{CO}_3 + \text{KNO}_3$) to bring them into solution. The solubility of the salts depends upon the charge to size ratio of the metal ions and also on the lattice. Table 2.9 gives some idea regarding the solubility of salts in water.

You will learn in detail about the various aspects of qualitative analysis in your practical classes.

SELF ASSESSMENT QUESTIONS

Multiple Choice questions

2.1 Put a tick (✓) mark against the suitable choice:

- (i) Which of the following metals is extracted by smelting ?
(a) sodium, (b) calcium, (c) copper, (d) aluminium
- (ii) Which of the following minerals/ores is not an oxide ?
(a) bauxite, (b) haematite, (c) cuprite, (d) calamine
- (iii) Which of the following statements is wrong ?
(a) Froth flotation method is employed for the concentration of ores.
(b) Limestone functions as flux in the blast furnace.
(c) Malachite is an ore of iron.
(d) Iron immersed in copper sulphate solution is rapidly coated with copper.
- (iv) A blast furnace is used in the extraction of :
(a) iron, (b) zinc, (c) aluminium, (d) calcium.
- (v) A substance used in metallurgy to remove rocky materials is called
(a) slag, (b) flux, (c) oxidizing agent, (d) gangue
- (vi) Extraction of metals from sulphide ores is accomplished by
(a) froth flotation process, (b) smelting process,
(c) electrolytic reduction, (d) thermal decomposition.
- (vii) The compound which gives off oxygen on moderate heating is (IIT 1986)
(a) cupric oxide, (b) mercuric oxide, (c) zinc oxide, (d) aluminium oxide
- (viii) In the electrolysis of alumina, cryolite is added to (IIT 1986)
(a) lower the melting point of aluminium.
(b) increase the electrical conductivity
(c) minimize the anode effect.
(d) remove impurities.
- (ix) Which of the following alkali metals is the most abundant in the earth's crust ?
(a) lithium, (b) potassium, (c) rubidium, (d) caesium
- (x) Metallic magnesium is obtained by
(a) electrolysis of molten magnesium chloride.
(b) reduction of MgO using coke as reducing agent.
(c) displacement of magnesium by iron from magnesium sulphate solution.
(d) none
- (xi) The chemical composition of cryolite mineral is,
(a) Na_3AlF_6 (b) $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (c) Al_2O_3 (d) KAlSi_3O_8
- (xii) Aluminium is not present in the mineral
(a) feldspar (b) fluorospar (c) cryolite (d) mica.
- (xiii) Industrially the most important mode of occurrence of iron in nature is as
(a) oxides, (b) sulphides, (c) carbonate, (d) sulphates
- (xiv) Copper occurs in
(a) native form (b) sulphide form (c) oxide form (d) native and combined form

- (xv) Calcination refers to
- heating of the ore strongly in the presence of air.
 - heating of the ore strongly in the absence of air.
 - heating of the ore in the presence of a metal.
 - purification of metals.

2.2 Fill in the blanks in the followings :

- The processes involved in the production of a metal from its ores are collectively known as.....
- The rocky material found with ores is known as
- The process in which the lighter gangue particles are washed away in a stream of water while the heavier minerals stay behind is known.....
- The method of removing volatile matter from ores is known as
- Roasting is a process in which.....
- In electrolytic refining, pure metal is deposited on the.....
- The element recovered from sea water on industrial scale is.....
- Sulphide ores are, generally, concentrated by.....process.
- The solid phase of the earth is called.....
- In extractive metallurgy of zinc, partial fusion of ZnO with coke is calledand reduction of the ore to the molten metal is called.....

2.3 Match the statements given in column (B) against the terms in column (A).

Column (A)	Column (B)
1. Iron	(i) Extracted from bauxite
2. Aluminium	(ii) Most abundant in earth's crust
3. Thermal decomposition	(iii) Effective in the extraction of mercury
4. Oxygen	(iv) Electrolytic reduction is used.
5. Lead	(v) Remains associated with silver as an impurity
6. Calamine	(vi) Ore of mercury
7. Cinnabar	(vii) Exists as carbonate in the earth's crust.
8. Calcination	(viii) A method of purification
9. Cupellation	(ix) A method of converting ore to oxide
10. Magnesium	(x) Extraction is accomplished in a blast furnace.

2.4 Which of the following statements are True (T) or False (F) ?

- Titanium is the most abundant element.
- Most of the metals occur in nature associated with electronegative elements.
- Rocks do not constitute the earth's crust.
- Sedimentary rocks are formed as a result of weathering processes
- Garnet represents igneous rocks.
- Calcination precedes smelting.
- Gangue is always a unusable mass.
- A mineral is a specific entity.
- Dressing of ore is not always required.
- Leaching is not an effective way of purifying ores.
- Ilmenite is a source of iron.
- Any mineral can be used for the extraction of a metal.

SHORT ANSWER QUESTIONS

2.5

- Name two naturally occurring substances with their chemical formulae for each of the metals : sodium, calcium, aluminium, iron, copper and zinc.
- Name three types of ores from which metals are extracted.

- (c) Comment on the followings:
1. In the extraction of aluminium from bauxite, CaF_2 is also used.
 2. Sodium is not found in its native state.
 3. Some metals occur in the native state.
 4. Sodium is deposited at the cathode during electrolytic dissociation of molten sodium chloride.
- (d) Name the ore and the process employed for the extraction of the following metals :
 (i) sodium, (ii) calcium, (iii) aluminium (iv) copper (v) zinc, and (vi) iron.
- (e) Which of the two metals in each of the following reactions is more reactive ?
 (i) $\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$
 (ii) $\text{CuO} + \text{Mg} \rightarrow \text{MgO} + \text{Cu}$
 (iii) $\text{Zn} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu}$
 (iv) $\text{Zn} + \text{Pb}(\text{CH}_3\text{COO})_2 \rightarrow \text{Zn}(\text{CH}_3\text{COO})_2 + \text{Pb}$
 Which characteristic property of metals makes them more reactive ?
- (f) Give a few properties of aluminium which make it industrially important.
- (g) Where are the deposits of copper, iron, zinc and aluminium found in India ?
- (h) For the reduction of the oxide to the metal suggest a reducing agent other than carbon and carbon monoxide.
- (i) Name the metal that can be extracted from the following:
 (a) Malachite, (b) Azurite, (c) Calamine, (d) Dolomite, (e) Phosphorite, and (f) Haematite

TERMINAL QUESTIONS

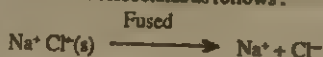
- 2.1 Explain the followings :
- (a) Any ore of a metal can be called mineral ?
 - (b) Froth flotation process of concentrating the ore is chiefly used for sulphides.
 - (c) Antimony can be obtained directly from its sulphide by treating it with iron.
 - (d) Thermal decomposition of mercurous oxide gives mercury.
- 2.2 In the smelting of oxide with carbon, explain the following observations made :
- (a) Carbon monoxide is an effective reducing agent.
 - (b) Carbon is not used in the reduction of chromic oxide.
 - (c) Both carbon monoxide and water gas are used for reduction.
 - (d) Carbon gets oxidized to both carbon monoxide and carbon dioxide.
 - (e) Reduction are carried at high temperatures.
- 2.3 Which of the following elements would you expect to exist in the combined form, which only in the native state and which, hardly at all ? Ag, Cr, Fr, Rn, Br, Mg, Hg and Ti. Give reasons for your findings.
- 2.4 Comment on the followings :
- (a) Electrode potential of a metal is a measure for deciding the method to be used for the extraction of that metal.
 - (b) In the electrolytic refining and electrolytic reduction processes the following observations are made :
 (i) The cathode is made out of the pure sample of the metal to be purified. The electrolyte used is also the soluble salt of that metal.
 (ii) At times, only anodes are dipped into molten metal salt or oxide.
 (iii) Iron and zinc ions from the solutions are not discharged at cathode along with copper.
- 2.5 (a) How has the problem of high temperatures been solved in the electrolytic reduction ?

- (b) Why do both iron and aluminium exist as oxides on the earth ?
 (c) Why do copper, lead, etc., exist as sulphides in the earth's crust ?
- 2.6 (a) Titanium is about 100 times more abundant in the earth's crust than copper, yet copper is available in plenty as a metal. why ?
 (b) Dissolution of the impurities in the molten metal help in getting the highly pure sample. Comment.
- 2.7 (a) Write chemical equations to represent the following processes :
 (i) Deposition of copper from an aqueous solution of Cu^{2+} ,
 (ii) Roasting of malachite, $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$, and
 (iii) Reduction of Fe_2O_3 using coke as a reducing agent.
 (b) Why should a metal as prevalent in nature as iron be so rarely found in a free state ?
- 2.8 (a) Name three steps involved in isolating metals from their ores.
 (b) Name three types of compounds which are very common to many metallic ores.
- 2.9 (a) Name some uses of the slag produced in a metallurgical operation - blast furnace.
 (b) name the term assigned to the elements along with the borderline between the true metals and the non-metals.
 (c) Name the three parts of earth's crust with their approximate compositions.
 (d) On roasting of an ore of a metal, generally, an oxide is obtained but cinnabar on roasting gives mercury metal. Explain
- 2.10 Discuss the following terms : (a) Metallurgy, (b) Smelting, (c) Flux, (d) Slag, (e) Leaching, and (f) Oxidative refining.
- 2.11 Usual methods of extraction are not employed for the extraction of groups 1 and 2, metals. Explain.
- 2.12 What is ore dressing ? Discuss the various methods used in ore dressing.
- 2.13 Name the process in which both reduction and refining are accomplished in a single operation. Which metal is extracted by this process ? Give the details of this process used in the extraction of that metal.
- 2.14 Mention the principles involved in the following processes :
 (a) Van Arkel method, (b) Mond's process, (c) Lavigation, (d) Zone refining, (e) Vacuum arc refining, and (f) Liquefaction
- 2.15 Outline the procedure for removing impurities in the following cases :
 (a) Cuprous sulphide left in the isolation of copper
 (b) Traces of lead contained by silver metal
 (c) Silver and gold accompanying copper
 (d) Carbon present in the pig iron
 (e) Cadmium present with zinc
 (f) Silica present in mercury
- 2.16 State and explain the principles involved in the isolation of the following metals : (a) Magnesium from carnallite, (b) Antimony from stibnite, (c) Aluminium from bauxite, (d) Chromium from chromite, (e) Silver from argentite, and (f) Mercury from cinnabar.
- 2.17 Write explanatory notes on : (a) Froth flotation process, (b) Cyanide process, (c) Oxidative refining, and (d) Classification of rocks.

- 2.18 (a) State the meaning of slag, gangue and flux. Give the relationship between them with examples.
 (b) Name the various methods used in refining of the metals. Substantiate your answer by taking one example for each.
- 2.19 State briefly the various processes employed in the isolation of metals from their ores. Illustrate your answer by taking two examples.
- 2.20 What are the various forms in which elements are found in nature ?

ANSWERS TO SELF ASSESSMENT QUESTIONS

- 2.1 (i) c, (ii) d, (iii) c, (iv) a, (v) b, (vi) b, (vii) b, (viii) a, b (ix) b, (x) a, (xi) a, (xii) b, (xiii) a, (xiv) d, (xv) b.
- 2.2 (i) metallurgy, (ii) gangue or matrix, (iii) hydraulic washing, (iv) calcination, (v) ore is heated in presence of air (vi) cathode, (vii) sodium, (viii) froth flotation (ix) lithosphere (x) sintering, smelting.
- 2.3 1. (x), 2. (i), 3. (iii), 4. (ii), 5. (v), 6. (vii), 7. (vi), 8. (ix), 9. (viii), 10. (iv)
- 2.4 (a) F, (b) T, (c) F, (d) T, (e) T, (f) T, (g) F, (h) T, (i) T, (j) F, (k) F, (l) F.
- 2.5 (a) Sodium : Rock salt from sea water, NaCl ; Chile salt petre, NaNO_3 .
 Calcium : Limestone, CaCO_3 ; Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
 Aluminium : Bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$; Felspar, KAlSi_3O_8
 Iron : Haematite, Fe_2O_3 ; Iron pyrites, FeS_2
 Copper : Copper pyrites, CuFeS_2 ; Malachite $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$
 Zinc : Zinc blende, ZnS ; Calamine : ZnCO_3
- (b) (i) Oxide, (ii) Sulphide, and (iii) Carbonate
- (c) 1. Calcium fluoride is used to lower down the melting point of alumina. It works as flux.
 2. Sodium is a highly reactive substance, and hence, is not found in its native state.
 3. Metals like, Ag, Au, Pt, etc., are not reactive and, hence, they are found in the native state.
 4. Sodium chloride dissociates as follows :



Sodium ions, because of their positive charge, move towards cathode and are reduced there. Finally they deposit on the cathode.



(Discharged on the cathode) (Deposited on the cathode)

- (d) (i) Rock salt or NaCl from sea water; Electrolytic dissociation of molten sodium chloride or sodium hydroxide
 (ii) Calcium chloride from sea water; Electrolytic dissociation of a mixture of calcium chloride and calcium fluoride.
 (iii) Bauxite; Electrolytic dissociation of a mixture of alumina (from bauxite) and cryolite (purified naturally occurring substance)
 (iv) Copper pyrites; Sulphide ore is crushed, concentrated and then roasted. The roasted ore is then smelted in the blast furnace. In smelting, roasted ore, i.e., oxide is reduced to metal.

- (v) Zinc blende; Sulphide ore is crushed concentrated and then roasted. During roasting a small amount of zinc sulphate is also formed along with oxide. The oxide is reduced with powdered coal in fire clay retorts (smelting)
- (vi) Haematite; Purified oxide is put to smelting in the blast furnace.
- (e) (i) Al, (ii) Mg, (iii) Zn, and (iv) Zn, Tendency to lose electrons. Greater the tendency of the metal to lose electrons the more reactive it is.
- (f) (i) Light metal, (ii) good conductor of heat and electricity, (iii) strong affinity for oxygen even at ordinary temperature, and (iv) corrosion resistant due to Al_2O_3 layer.
- (g) Copper (as sulphide) : Singhbhum (Bihar) and Katni (Rajasthan)
 Iron (in haematite) : Singhbhum (Bihar), Orissa, West Bengal, Mysore (Karnataka) Zinc (as sulphide) : Udaipur (Rajasthan)
 Aluminium (in bauxite) : Bihar, Orissa, Andhra Pradesh, Tamil Nadu.
- (h) - Aluminium powder
- (i) (a) Copper, (b) Copper, (c) Zinc, (d) Calcium, (e) Calcium and (f) Iron.

UNIT - 3

States of Matter

..... it is my intention to make known some new properties in gases, the effects of which are regular, by showing that these substances combine amongst themselves in very simple proportions

JOSEPH L. GAY-LUSSAC

UNIT PREVIEW

- 3.1 Introduction
- 3.2 The gaseous state
 - 3.2.1 Measurable properties of gases
- 3.3 Behaviour of gases
 - 3.3.1 Boyle's law
 - 3.3.2 Charles' law
 - 3.3.3 Absolute scale of temperature
 - 3.3.4 Gay-Lussac's law
 - 3.3.5 Avogadro's hypothesis
 - 3.3.6 Dalton's law of partial pressure
- 3.4 Ideal gas equation
- 3.5 STP and molar volume
- 3.6 Kinetic molecular theory of gases
 - 3.6.1 Kinetic gas equation
 - 3.6.2 The relation between kinetic energy and absolute temperature
 - 3.6.3 Boyle's law from kinetic gas equation.
 - 3.6.4 Charles' law from kinetic gas equation
 - 3.6.5 Avogadro's law from kinetic gas equation
 - 3.6.6 Graham's law of gaseous effusion from kinetic gas equation
 - 3.6.7 Dalton's law of partial pressures from kinetic gas equation
- 3.7 Kinetic energy of an ideal gas
- 3.8 Calculation of molecular velocities
- 3.9 Ideal gases and real gases
 - 3.9.1 Deviations of real gases from gas laws
 - 3.9.2 The causes of deviation from ideal gas laws
 - 3.9.3 van der Waal's equation
- 3.10 The solid state and its characteristics
- 3.11 The crystal lattice (or space lattice)
- 3.12 Types of solids
- 3.13 X-Ray diffraction studies
- 3.14 Crystal lattices (systems) and unit cells
- 3.15 Packing of constituent particles in crystals
- 3.16 Properties of liquids
- Self assessment questions
- Terminal questions
- Answers to self assessment questions

LEARNING OBJECTIVES

After completing this unit you should be able to

1. Explain the working of a mercury barometer an open-end manometer.

2. Understand, for a fixed mass of a gas at constant temperature, volume changes with pressure or vice-versa. (Boyle's law)
3. Calculate the volume change with temperature or vice-versa for a fixed amount of a gas at constant pressure (Charles' law)
4. Convert temperature on absolute scale from other scales of temperature measurement.
5. Understand the relationship between pressure and temperature of a gas for its constant volume
6. Calculate volume of a gas from number of molecules (or moles) of a gas (Avogadro's law).
7. Calculate the total pressure exerted by a mixture of gases from the partial pressures of the gases present in the gaseous mixture (Dalton's law of partial pressures)
8. Use the ideal gas equation for calculating pressure, volume or temperature of a gas when the values of any other two variables are given.
9. State the basic assumptions of the kinetic molecular theory.
10. Calculate the average kinetic energy of a fixed quantity of a gas at a certain temperature.
11. Deduce the various gas laws with the help of kinetic molecular theory.
12. Calculate molecular speed of gas molecules.
13. Explain why gases deviate from ideal behaviour- van der Waal's equation.
14. Describe the common type of intermolecular forces and how these forces influence the physical properties of a substance.
15. Understand the geometrical arrangement of simple crystals.
16. Describe how crystal structures can be related to the close packing of spheres.

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3.1 INTRODUCTION

The physical classification of matter divides it into three forms-solid, liquid and gas. The macroscopic examination of matter revealed that the three forms of matter have different physical properties.

A comparison of the physical properties of three states are given in Table 3.1.

TABLE 3.1 Comparison of the physical properties of gases, liquids and solids

Properties	Gas	Liquid	Solid
Particle arrangement	Widely separated	Separated with small distance	Closely packed together
Shape	Acquires shape of the container	Acquires shape of its own	Definite shape of its own
Volume	No volume of its own	Definite volume	Definite volume
Diffusion	Easy	Slower than gases	Very slow
Compressibility	Easy	Difficult	very difficult
Density	Low	High	High
Mixability	Readily	Slower than gases	Extremely slow

3.2 THE GASEOUS STATE

Historically gaseous state of matter was the first state which was studied in detail. Apart from the properties of gases given in Table 3.1, the

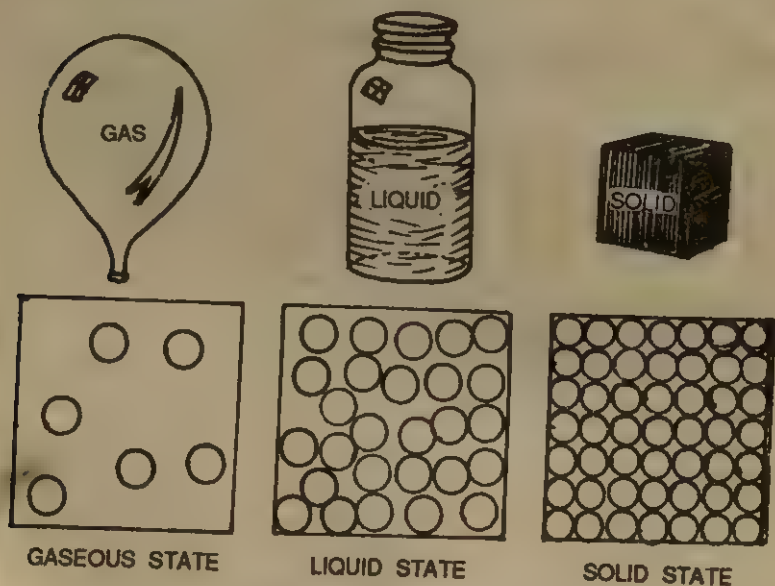


Fig. 3.1 The three states of matter

gases were characterised by certain quantitative relationships between its mass, volume, density, temperature, pressure etc. Although it is very difficult to handle gases, it is quite important to know how to measure the properties.

3.2.1 Measureable Properties of Gases

In the study of gases, it is important to measure the mass, volume, temperature and pressure of a gas.

(i) **Mass** : The mass of a gas contained in a vessel is very small. Though mass of a gas can be determined by weighing the container empty and then filling it with the gas. How to weigh an empty container ? You have read that gases are collected either by displacement of water or air. In former case, mass of a gas can be determined by simple weighing. For the gases which are soluble in water, rubber balloons are used to find the mass of a given amount of the gas by difference weight method. In this method, following observations are made:

Mass of the empty balloon = a g

Mass of the balloon filled with gas = b g

Mass of gas in the balloon = $(b-a)$ g

The number of moles of the gas can be related with its mass.

$$\text{Number of moles (N)} = \frac{\text{Mass of the gas (M)}}{\text{Molar mass of the gas (M)}}$$

(ii) **Volume** : The volume of a gas is the amount of space occupied by it. A gas fills completely any container in which it is kept. So the volume of the gas will be taken as the volume of the container.

Gases are completely miscible. If two or more gases are mixed together in a container of fixed dimensions, the volume of the gas mixture is still equal to the volume of the container. The volume of a mixture of gases is independent of the original volumes of individual gases.

The SI unit of volume is m^3 . The smaller units are dm^3 and cm^3 .

$$1 \text{ m}^3 = 10^3 \text{ dm}^3 = 10^6 \text{ cm}^3$$

However, it is quite often that volume is measured and expressed in litres or millilitres.

$$1 \text{ litre (1L)} = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$$

$$1 \text{ millilitre (1mL)} = 1 \text{ cm}^3 = 10^{-3} \text{ dm}^3 = 10^{-6} \text{ m}^3$$

(iii) **Temperature** : Gases exhibit same properties of heat transfer as that of liquids for solids. A thermometer immersed in a gas, will register its temperature. Mercury thermometers are generally used to measure temperature in the vicinity of room temperatures. Temperatures are generally represented on the three scales, viz., the Fahrenheit ($^{\circ}\text{F}$), the Celsius ($^{\circ}\text{C}$) and the Kelvin (K) scale. The SI unit of temperature is Kelvin. In all the temperature scales,

the freezing and boiling temperatures of water at one atmosphere pressure are taken as standard (Fig 3.2). While the difference of the two points is 100° on the Celsius and the Kelvin scale, it is 180° on the Fahrenheit scale. The three temperature scales have the following correlation :

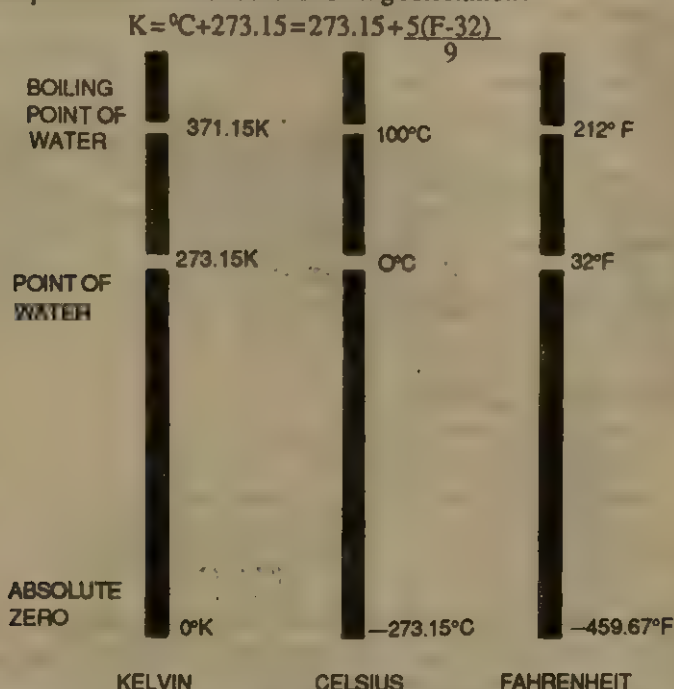


Fig. 3.2 Comparison of temperature scale

(iv) **Pressure** : Gas molecules are always in a state of motion. When they strike on the walls of the container, a definite force is exerted by the transfer of momentum. The pressure exerted by a gas is equal to the force per unit area.

Pressure is measured by the flow of mass that normally moves from regions of high pressure to low pressure. Torricelli (1608-1647) developed mercury barometer which is used to measure the pressure of a gas. The mercury barometer consists of a long glass tube (76cm) closed at one end, which is filled with mercury and inverted in a vessel of mercury (Fig. 3.2). When tube is inverted, some of the mercury runs out of the tube. The height of mercury column which remains in the inverted tube is found to be independent of length and cross-sectional area of the tube and the shape and size of the vessel containing the mercury. The height of the mercury column serves as the measure of atmospheric pressure.

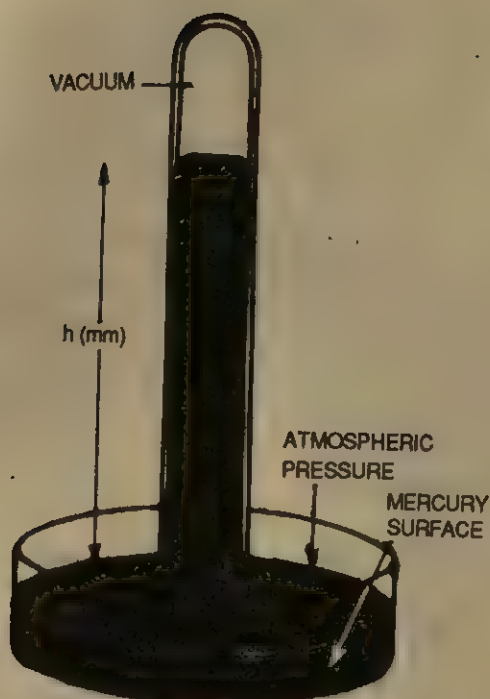


Fig. 3.3 The barometer

Pressure is expressed as force per unit area. The force exerted by a mercury column of height, 'h', and of cross-section area, A, will be proportional to the mass of mercury supported in the column.

Let the pressure be P,

$$P = \frac{\text{Force}}{\text{Area}} = \frac{\text{Mass} \times \text{Acceleration}}{\text{Area}} \quad (3.1)$$

$$\text{or } p = \frac{mg}{A} \quad (3.2)$$

where m is the mass of mercury in the tube and g is acceleration due to gravity. Mass can be correlated with volume and density as,

$$\text{Mass} = \text{Volume} \times \text{density}$$

If ρ is the density of mercury and V is the volume of mercury then,

$$p = \frac{\rho Vg}{A} \quad (3.3)$$

But, in the column $V = A \times h$

Hence,

$$P = \rho \cdot hg \quad (3.4)$$

Pressure is generally expressed in atmosphere (atm). By international agreement, one atmosphere is the pressure exerted by a column of 76 cm of

mercury. It is the pressure due to atmosphere at sea level at 273K. The other units of pressure are mm of Hg or torr. The SI unit of pressure is pascal which is equal to the pressure exerted by one newton force when it acts on an area of one square metre. The equivalence of various units of pressure are,

$$1 \text{ atm} = 760 \text{ mm of Hg} = 760 \text{ torr} = 101.325 \text{ kPa}$$

For approximate work, one atmosphere may be taken equal to 10^2 kPa or 10^5 Pa .

Manometer : The pressure of a gas in a closed container is generally measured with the help of a manometer (Fig. 3.4). It essentially consists of a U-tube, one end of which is fitted with a stop-cock and the other end is kept open. The mercury is filled in the U-tube. The stop-cock end is connected to the container and the stop-cock is opened by noting the difference of height of mercury level in U-tube, the pressure of the gas in the container can be calculated.

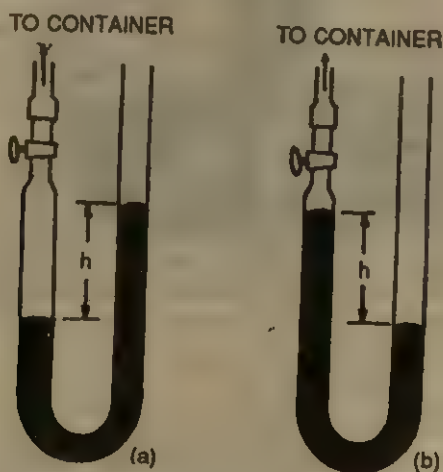


Fig. 3.4 Measuring pressure with a mercury manometer

Let the atmospheric pressure be 760 mm of Hg.

When height of the column open to the atmosphere is more (Fig. 3.3 (a)) the pressure of the gas will $760+h$ mm of Hg. If the height of mercury in the column open to the atmosphere is less (Fig. 3.3 b), then the pressure of the gas is less than the atmospheric pressure and is equal to $760-h$ mm of Hg.

3.3 BEHAVIOUR OF GASES

3.3.1 Boyle's Law

Robert Boyle (1627-1691) was an English scientist. He investigated the relationship between volume and pressure in the given mass of a gas at constant temperature. Figure 3.5 illustrates, how the volume of a given mass of a gas varies with change in its pressure.

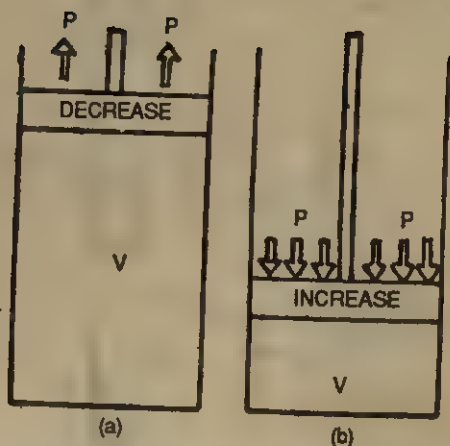


Fig. 3.5 (a) When the pressure decreases the volume increases, and (b) when the pressure increases the volume decreases.

Robert Boyle experimented with the compressibility of air using an apparatus shown in Fig. 3.6. Fixed quantity of a gas is taken in a cylinder with movable piston and the pressure is read on the manometer by changing its volume. It is found that as the volume is reduced to $2/3$ rd the pressure increased 1.5 times.

A generalization concerning the relation between volume and pressure of a given mass of a gas is known as Boyle's law. It states that the volume of a given mass of any gas at constant temperature varies inversely with pressure, i.e.,

$$V \propto \frac{1}{P} \quad (3.5)$$

$$\text{or } PV = \text{constant} \quad (3.6)$$

$$\text{or, } P_1 V_1 = P_2 V_2 \text{ given}$$

Boyle's law can be readily depicted graphically. Figure 3.7 represents the variation of the volume of a given amount of a gas with pressure when the temperature is kept constant.

From the graphs it is clear that as the gas pressure increases the volume decreases in such a way that the product of P and V remains constant (Fig. 3.8).

The pressure-volume correlation under two different sets of conditions for a fixed mass of a gas at constant temperature may be written as,

$$P_1 V_1 = P_2 V_2 \quad (3.7)$$

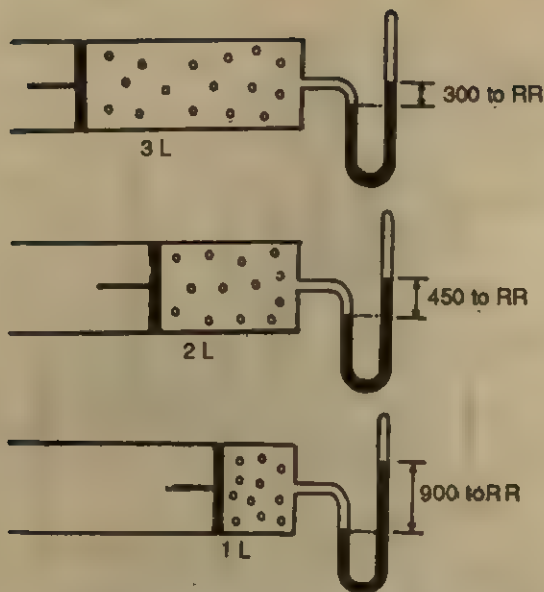


Fig. 3.6 Apparatus to illustrate Boyle's law

Where P_1 and P_2 are the pressures at which volume of the gas are V_1 and V_2 respectively.

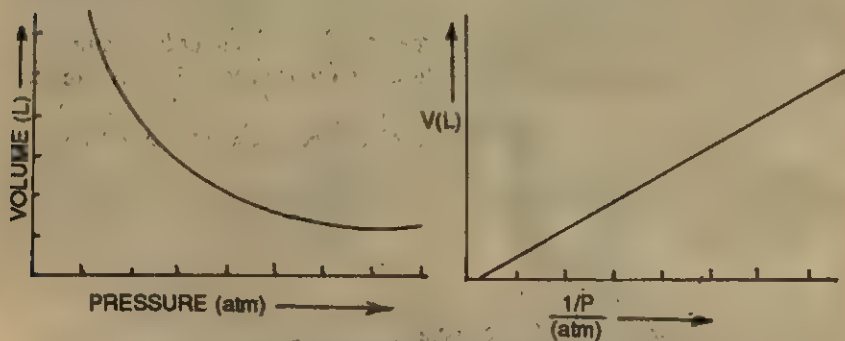


Fig. 3.7 Graphical representation of Boyle's law

The Boyle's law expresses that the gases are compressible. When a fixed mass of a gas is under high external pressure, the molecules contained in the gas occupy less space i.e., the gases become denser under pressure. A direct consequence of this is seen in the atmosphere. At sea level, the air is dense while its density and pressure decreases as we go at high altitude. At Mount Everest, the pressure is approximately half of that at the sea level. At high altitude, as the pressure is low, it causes altitude sickness (sluggish feeling, headache) due to decrease in oxygen intake. Mountain climbers and the soldiers guarding our frontiers in Ladakh undergo extensive training to adapt their bodies to the low oxygen pressure. In addition, they also carry

oxygen gas cylinders with them for an emergency. Similarly, the interiors of jet airplanes, space-craft etc. which normally fly at high altitudes, are specially maintained at normal pressure and are equipped with emergency oxygen supply in case pressure falls.

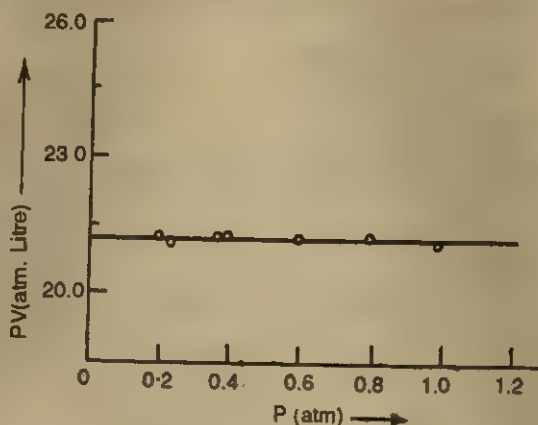


Fig. 3.8 Plot of PV vs P

Exercise 3.1: A weather balloon has a volume of 175 L when filled with hydrogen at 1 atm pressure. Calculate the volume of the balloon when it rises to a height of 3000m where the atmospheric pressure is 0.75 atm. and temperature remains constant.

Solution: We know, $P_1 V_1 = P_2 V_2$
 $1 \text{ atm} \times 175 \text{ L} = 0.75 \text{ atm} \times V_2$
 $V_2 = \frac{175 \times 1}{0.75} = 233.3 \text{ litres}$

Exercise 3.2: A gas jar fitted with a piston contains 20 litres of nitrogen gas when the pressure is 1 atm. By applying additional pressure, the gas is compressed to 12.5 litres. How much amount of additional pressure is exerted on the piston?

Solution:

$$P_1 V_1 = P_2 V_2$$

$$20 \times 1 = P_2 \times 12.5$$

or $P_2 = \frac{20}{12.5}$

$$= 1.6 \text{ atm.}$$

Additional pressure = $1.6 - 1 = 0.6 \text{ atm.}$

3.3.2 Charles' Law

Gases expand when heated under constant pressure and contract when cooled. This can be easily observed with the help of a balloon filled

with air. When the balloon is placed in hot water, it expands while in ice, it contracts. The changes in the volume of a gas with temperature were carefully studied by Jacques Charles and in 1787 he gave a law known as Charles' law. Charles' law can be stated as: the volume of a fixed mass of a gas at constant pressure is directly proportional to its temperature in Kelvin, i.e.

$$V \propto T \text{ or } \frac{V}{T} = \text{constant} \quad (3.8)$$

$$\text{or } \frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (3.9)$$

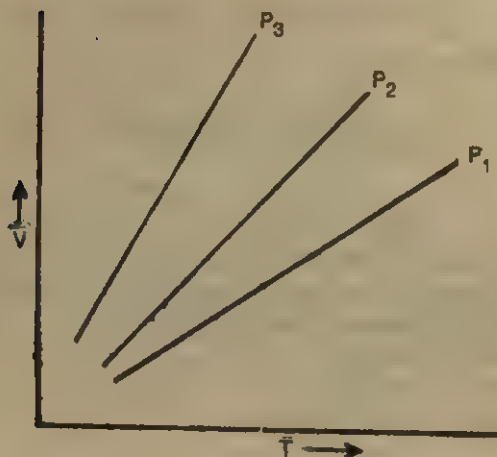


Fig. 3.9 Charles' law-plot of V (mL) vs. T (K) at constant pressure P (atm)

Charles' law can be readily described graphically. Figure 3.10 represents the variation of the volume of a given amount of gas with temperature when the pressure is held constant. For different pressures different plots are obtained ($P_1 > P_2 > P_3$). From the graph it is clear that as the temperature increases the volume also increases in such a way that V/T remains constant.

All gases do not follow this trend closely at all the temperatures. A gas which obeys both Boyle's law and Charles' law is said to behave ideally.

Joseph Gay-Lussac (1802) studied the effect of temperature on the volume of a gas quantitatively. He found out that the ratio of volumes of air or any other gas at 100°C and 0°C is always a constant which is independent of initial volume provided pressure remains constant.

Experimental observations revealed that

$$\frac{V_{100}}{V_0} = 1.366 \quad (3.10)$$

or

$$V_{100} = 1.366 V_0 \quad (3.11)$$

$$= V_0 + 0.366 V_0 \quad (3.12)$$

Here V_{100} and V_0 are the volumes of the gas at 100°C and 0°C .

It has also been observed that the expansion of gas is uniform over the range of temperature.

This means that expansion of a gas per unit degree will be given by $\frac{0.366}{100} V_0$

which is equal to $\frac{1}{273} V_0$. Thus, for each degree rise in temperature, the

volume of a gas will increase $1/273$ time its volume at 0°C .

$$V_t = V_0 (1 + t/273) \quad (3.13)$$

Figure 3.10 shows the variation in volume with temperature.

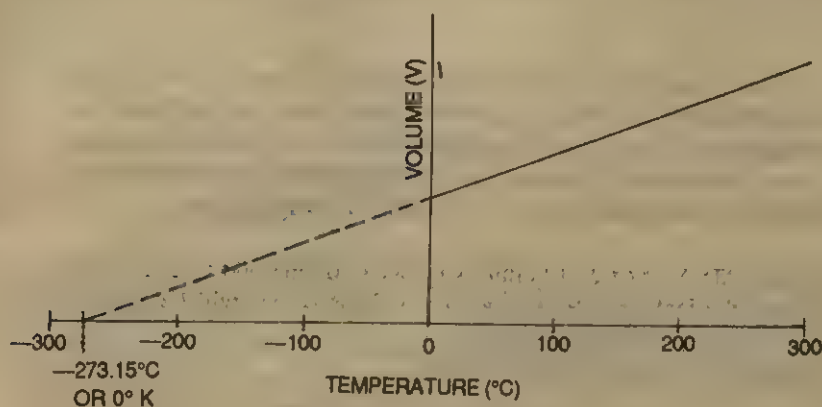


Fig. 3.10 Plot between volume and temperature at constant pressure

3.3.3 Absolute Scale of Temperature

Gay Lussac noted that the volume of a gas decreases by $1/273$ times of its volume at 0°C with the decrease of 1°C in temperature. What will happen if we go on decreasing the temperature? The volume of gas will go on decreasing, is the obvious answer. If this happens, then the volume of a gas will become zero at -273°C .

Substituting -273 for t in equation (3.13), we have

$$V_t = V_0(1 - 273/273) = 0 \quad (3.14)$$

The temperature at which volume of an ideal gas becomes zero is known as *absolute zero temperature*. It is interesting to note that this is the lowest possible temperature which can be attained. The study of cryogenics has made it possible to reach up to -272.63°C . Lord Kelvin (1848) proposed a temperature scale taking this absolute zero as the reference. The temperature for one degree on the Celsius scale is equal to the one degree on the Kelvin scale. The temperature of Celsius scale can be easily converted to Kelvin scale by adding 273 to Celsius scale reading,

$$K = ^\circ\text{C} + 273 \quad (3.15)$$

More precise determinations have revealed that absolute zero on Celsius scale should be at -273.15° . Using Kelvin scale, the variations in the volume of a definite mass of gas with temperature can be given by a mathematical expression,

$$V \propto T \quad (3.16)$$

Where $T = t + 273$, temperature on Kelvin scale and pressure is maintained constant. The expression at two different temperatures will be,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (3.17)$$

Though absolute scale of temperature is based on the concept that the volume of a gas will be zero at 0K but it is not possible to attain 0K in practice. All the gases condense to liquid and solid before this temperature is attained. However, concept of absolute zero is very useful in all scientific work. This scale is also known as *thermodynamic scale of temperature*.

Exercise 3.3: A sample of helium gas has a volume 500 cm^3 at 100°C . Calculate the temperature at which the volume of gas will be 260 cm^3 . Assume the pressure remains constant.

Solution: According to Charles' Law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Given: $V_1 = 500\text{ cm}^3$

$$T_1 = 273 + 100 = 373\text{ K}$$

$$V_2 = 260\text{ cm}^3$$

$$T_2 = ?$$

Substituting the values,

$$\frac{500}{373} = \frac{260}{T_2}$$

$$\text{or } T_2 = \frac{260}{500} \times 373 = 1934\text{ K}$$

3.3.4 Gay-Lussac's Law

Gay-Lussac also studied the effect of temperature on the pressure of a gas when it has fixed volume and mass. He proposed that the pressure exerted by a given mass of a gas having fixed volume is directly proportional to absolute temperature. Mathematically,

$$P \propto T \quad (3.18)$$

or

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad (3.19)$$

Exercise 3.4 : A certain amount of gas when filled in a closed steel container exerts a pressure of 750 torr at 27°C. Calculate the pressure when temperature of the gas is raised to 400K.

Solution: We have,

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\text{Given, } P_1 = 750 \text{ torr, } T = 273 + 27 = 300\text{K}$$

$$T_2 = 400\text{K } P_2 = ?$$

Substituting the values,

$$\frac{750}{300} = \frac{P_2}{400}$$

or

$$\begin{aligned} P_2 &= 250 \times 4 \\ &= 1000 \text{ torr.} \end{aligned}$$

3.3.5 Avogadro's Hypothesis

Amedeo Avogadro (1776-1856) was an Italian scientist. He too believed in the earlier hypothesis of equal number of particles in equal volumes of gases but he solved the difficulty by approaching the problem in another way and enunciated his famous law known as Avogadro's law, i.e. :

Equal volumes of all gases under similar condition of temperature and pressure, contain equal number of molecules.

The greatest importance of Avogadro's law is that it gives a method of obtaining the relative weights of molecules. The weight of a gas sample is the number of molecules in the sample multiplied by the weight of each molecule, i.e., weight = number of molecules \times weight of one molecule. If samples of hydrogen and oxygen having the same volume, temperature and pressure are weighed, the sample weights have the ratio,

$$\left(\frac{\text{weight of hydrogen}}{\text{weight of oxygen}} \right) \quad \text{same } V, T, P$$

$$\frac{\text{number of molecules of hydrogen} \times \text{weight of one hydrogen molecule}}{\text{number of molecules of oxygen} \times \text{weight of one oxygen molecule}} \quad (3.20)$$

But since the number of hydrogen molecules is the same as the number of oxygen molecules by Avogadro's hypothesis, the number terms cancel out and we are left with,

$$\left(\frac{\text{weight of hydrogen}}{\text{weight of oxygen}} \right)_{V,T,P} = \frac{\text{weight of one H}_2 \text{ molecule}}{\text{weight of one O}_2 \text{ molecule}} \quad (3.21)$$

3.3.6 Dalton's Law of Partial Pressure

Partial Pressure

Experiment 3.1: Take three 1L flasks A, B and C (Fig. 3.11) at 298 K. The flask, A, contains 0.01 mole of nitrogen. The manometer shows that pressure

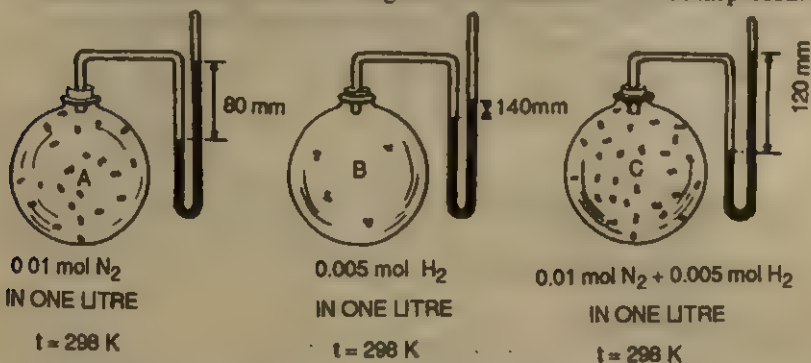


Fig.3.11 Pressure of a mixture of gases

is 80 mm Hg. The flask B contains 0.005 mole of hydrogen. The pressure in this flask is 40 mm Hg. The third flask C contains 0.01 mole N₂ and 0.005 mole H₂. The pressure in this flask is 120 mm Hg. From this Experiment, we can conclude that the pressure exerted by the mixture of nitrogen and hydrogen gases is just the sum of the pressure that nitrogen exerts when alone in the flask and the pressure that hydrogen exerts when alone in the flask. 120 mm Hg = 80 mm Hg + 40 mm Hg.

The pressure exerted by an individual gas in the mixture is called the partial pressure of that gas.

The partial pressure of a gas is the pressure that the gas would exert if it were alone in the container. In the above experiment, the partial pressures of nitrogen and hydrogen are 80 mm Hg and 40 mm Hg, respectively.

John Dalton stated law of partial pressures in 1801. The law states: The total pressure of a mixture of gases is equal to the sum of the partial pressures of each individual gas that makes up the mixture. Let a mixture contains three gases exerting partial pressures p_1 , p_2 and p_3 respectively. The total pressure P , exerted by the mixture of these gases is given by,

$$P = p_1 + p_2 + p_3 \quad (3.22)$$

3.4 IDEAL GAS EQUATION

The laws of Boyle and Charles can be combined to obtain a more general law for the behaviour of gases. Let P_1 , V_1 , T_1 and P_2 , V_2 , and T_2 be the pressure, volume and temperature in states 1 and 2 respectively of any definite quantity of a gas. This can be achieved in two steps:

Step 1: At constant temperature T_1 , when the pressure P_1 is changed to P_2 , the volume V_1 changes to V_x . According to Boyle's law:

$$P_1 V_1 = P_2 V_x \quad (3.23)$$

$$\text{or} \quad V_x = \frac{P_1 V_1}{P_2} \quad (3.24)$$

Step 2: At constant pressure P_2 , when the temperature T_1 is changed to T_2 , the volume V_x changes to V_2 . According to Charles' law:

$$\frac{V_x}{T_1} = \frac{V_2}{T_2} \quad (3.25)$$

$$\text{or} \quad V_x = \frac{T_1 V_2}{T_2} \quad (3.26)$$

From equations 3.24 and 3.26

$$\frac{P_1 V_1}{P_2} = \frac{T_1 V_2}{T_2} \quad (3.27)$$

$$\text{or} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = \text{constant, } k$$

$$\text{In general} \quad \frac{PV}{T} = k \quad (3.28)$$

Thus, for a given amount of a gas PV/T is constant. The numerical value of k depends on the amount of the gas but is independent of the nature of the gas. For one mole of a gas, the constant is referred to as the molar gas constant and is denoted by R .

$$\text{Therefore for one mole of a gas} \quad \frac{PV}{T} = R \quad (3.29)$$

where R is known as the gas constant. For n moles, equation (3.29) becomes

$$PV = nRT \quad (3.30)$$

This is called the ideal gas law. Numerical value of R depends on the units used for P , T , V and n . If volume is expressed in litres, pressure in atmospheres, temperature in Kelvin and n as the number of moles, then the unit of R will be,

$$R = \frac{PV}{nT} = \frac{\text{atm litre}}{\text{mole Kelvin}}$$

Equation 3.52 shows that the velocity of molecules of a gas depends only on its temperature besides its nature.

The equations (3.50), (3.51) and (3.52) or (3.53) are the working formulae for computing the velocities of gases. The choice of the equation will depend on the data given in a particular problem. This is illustrated by the following examples:

Exercise 3.12 : Calculate the root mean square velocity and average velocity of hydrogen molecules at STP

$$\text{Here } P = 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dynes/cm}^2$$

$$V = 22400 \text{ Mol}^{-1} \quad M = 2.016 \text{ g}$$

$$\text{From equation (3.50)} \quad C = \sqrt{3VP/M}$$

$$C = \sqrt{\frac{3 \times 76 \times 13.6 \times 981 \times 22400}{2.016}}$$

$$\text{Root Mean Square Velocity} = 183840 \text{ cms}^{-1}$$

$$\text{Average Velocity} = 0.921 \times \text{rms velocity}$$

$$\therefore U_{av} = 0.921 \times 183840 = 169320 \text{ cms}^{-1}$$

Exercise 3.13 : Calculate the root means square velocity of oxygen molecules at 15°C.

$$\text{From equation (3.53)} \quad C = 1.58 \times 10^4 \sqrt{\frac{T}{M}} \text{ cm/sec}$$

$$\text{Here } T = 273 + 15 = 288 \text{ K}$$

$$M = 32 \text{ g}$$

Substituting the values we have

$$C = 1.58 \times 10^4 \sqrt{288/32} \text{ cms}^{-1}$$

$$= 1.58 \times 10^4 \times \sqrt{9}$$

$$= 1.58 \times 10^4 \times 3$$

$$= 4.74 \times 10^4 \text{ cms}^{-1}$$

3.9 IDEAL GAS AND REAL GASES

So far it has been shown that gases do actually obey the gas laws. A close examination of experimental data of the real gases shows that this is so only at low pressures and moderately high temperatures. The equation $PV = nRT$, which is the consolidated expression of the gas laws, is followed only approximately by the real gases.

As the pressure is increased or the temperature is decreased, marked deviations from the laws become evident. It is clear that the gas equation cannot be regarded as correct for a real gas under all the conditions. An ideal or perfect gas is defined as a gas which strictly obeys the gas laws and for which the equation $PV = nRT$ holds good accurately. No such gas is known. However, the concept of an ideal or perfect gas, as a model has been useful for building up the equation of state for real gases. We have seen that the gas laws follow from the kinetic gas equation for the gases. This equation has been derived on the assumption amongst others that the inter molecular forces are absent in the gas. This may be true for an ideal or perfect gas but

atm litre per degree Kelvin per mole.

There are other ways also of expressing the unit of R .

Now the value of R can be calculated from the fact that 1 mole of every gas at STP occupies a volume of 22.4 litres.

$$R = \frac{1 \times 22.4}{273.15} = 0.0821 \text{ atm litre per mole per degree kelvin (3.31)}$$

3.5 STP AND MOLAR VOLUME

Standard temperature and pressure is abbreviated as STP. What volume does 1 mole of a gas occupy at STP ? This can be easily calculated by substituting the values of P , T and R in equation 3.30,

$$P = 1.00 \text{ atm} \quad T = 273 \text{ K}$$

$$n = 1.00 \text{ mol}$$

$$R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1}$$

in the relation $V = \frac{nRT}{P}$, We get

$$V = \frac{1 \times 0.0821 \times 273}{1}$$

$$= 22.4 \text{ litres}$$

Thus, 1 mole of an ideal gas will occupy a volume of 22.4 litres at STP. The value 22.4 litres per mole is called the molar volume of a gas and is valid at STP

Exercise 3.5 : A sample of nitrogen gas occupies a volume of 1.000L at a pressure of 0.5000 atm at 40°C. Calculate the pressure if the gas is compressed to 0.225 cm³ at -6°C.

Solution : We are given

$$P_1 = 0.5000 \text{ atm}$$

$$V_1 = 1 \text{ L} = 1000 \text{ cm}^3$$

$$T_1 = 40^\circ = 40 + 273.15 = 313.15 \text{ K}$$

$$P_2 = \text{To be determined}$$

$$V_2 = 0.225 \text{ cm}^3$$

$$T_2 = -6^\circ \text{ C} = 273.15 + (-6) \\ = 267.15 \text{ K}$$

Using combined gas law, i.e.,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$
$$P_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{V_2}$$

Substituting the values, we get

$$P_2 = \frac{0.5000 \text{ atm} \times 1000 \text{ cm}^3 \times 267.15 \text{ K}}{313.15 \text{ K} \times 0.225 \text{ cm}^3}$$

$$P_2 = 1.896 \times 10^3 \text{ atm}$$

Exercise 3.6 : A gas occupies a volume of 3.60 dm^3 at 298K and 2.49 atm . How many moles of gas are present in the sample?

Solution : $V = 3.60 \text{ dm}^3$; $T = 298\text{K}$

$$P = 2.49 \text{ atm}; n = ?$$

$$R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1}$$

Using ideal gas law,

$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{2.49 \times 3.60}{0.0821 \times 298}$$

$$= 0.366 \text{ mol}$$

Exercise 3.7 : Consider 325 litres sample of a gas at 298K and 750 mm of Hg. If the volume is changed to 315 litres and the pressure to 760 mm of Hg, what is the final temperature of the gas?

Solution : $P_1 = 750 \text{ mm}$, $P_2 = 760 \text{ mm}$

$V_1 = 325 \text{ litres}$ $V_2 = 315 \text{ litres}$

$T_1 = 298\text{K}$ $T_2 = ?$

According to the gas law,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{Substituting: } \frac{750 \times 325}{298} = \frac{760 \times 315}{T_2}$$

$$\text{or } T_2 = \frac{760 \times 315 \times 298}{750 \times 325}$$

$$= 293\text{K}$$

Exercise 3.8 : What is the volume occupied by 3.55g of chlorine gas at 50°C and 740 mm Hg ?

Solution : We know $PV = nRT$

$$\text{or } V = \frac{nRT}{P}$$

Substituting the values

$$V(\text{litre}) = \frac{3.55}{71} \text{ mol} \times 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 323.15\text{K}$$

$$\frac{740 \text{ atm}}{760}$$

$$= 1.36 \text{ L}$$

Exercise 3.9 : What is the molecular mass of a gas if 1.80g of it occupies a volume of 1.51L at 298K and 740 mm Hg ?

Solution:

$$P = 740 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = \frac{740 \text{ atm}}{760}$$

$$V = 1.51 \text{ L}$$

$$m = 1.81 \text{ g}$$

$$\text{Molecular mass} = M$$

$$T = 298 \text{ K}; R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$\text{We know } PV = nRT = \frac{m}{M} RT$$

$$\text{or } M = \frac{m}{PV} RT$$

Substituting the values

$$\begin{aligned} MW &= \frac{1.81 \text{ g} \times 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{\frac{740}{760} \text{ atm} \times 1.51 \text{ L}} \\ &= 30.1 \text{ g mol}^{-1} \end{aligned}$$

Exercise 3.10 : (i) What is the pressure exerted by a mixture of 1.1 g H_2 and 8.0 g O_2 when confined to a volume of 2.0 L at 27°C ?

(ii) Calculate the partial pressure of H_2 in the gaseous mixture

$$\text{Solution: } n_{\text{total}} = \frac{1.1 \text{ g } \text{H}_2 \times 1 \text{ mol } \text{H}_2}{2.0 \text{ g } \text{H}_2} + \frac{8.0 \text{ g } \text{O}_2 \times 1 \text{ mol } \text{O}_2}{32.0 \text{ g } \text{O}_2}$$

$$= 0.55 \text{ mol} + 0.25 \text{ mol}$$

$$= 0.80 \text{ mol}$$

$$\text{We know } PV = nRT$$

$$\text{or } P = \frac{nRT}{V}$$

Substituting the values

$$P = \frac{0.80 \text{ mol} \times 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{2 \text{ L}}$$

$$= 9.85 \text{ atm}$$

$$P_{\text{H}_2} = \frac{n_{\text{H}_2}}{n_{\text{total}}} \times P_{\text{total}}$$

$$= \frac{0.55 \text{ mol}}{0.80 \text{ mol}} \times 9.85 \text{ atm}$$

$$= 6.77 \text{ atm}$$

3.6 KINETIC MOLECULAR THEORY OF GASES

All the gas laws describing the behaviour of gases were arrived at by experiments. The kinetic theory of gases on the other hand tries to explain the behaviour of gases by theoretical means in terms of certain assumptions given below:

The following are the basic assumptions of the kinetic molecular theory:

1. A gas consists of a large number of tiny particles called molecules. Molecules of a gas are thought to be of the same size and mass but to differ from gas to gas.
2. The molecules are solid, spherical in shape and perfectly elastic. Therefore, there is no loss of kinetic energy when the molecules collide among themselves or with the walls of the container.

3. The molecules are in a state of constant rapid motion. They move in all the possible directions with all the possible speeds. There is no preferential direction for their motion. They move in a straight line till they collide with each other or with the walls of the container, then only the direction of their motion is changed. At any particular time different molecules in a gas have different speeds. This speed of molecules keeps on changing because of collision among themselves. However, at a particular temperature this distribution of speeds remains constant.

Figure 3.13 shows the distribution of velocities at two different temperatures. These curves are known as Maxwell - Boltzmann distribution curves.

Figure 3.14 gives the percentage of molecules having a particular velocity at a constant temperature.



Fig. 3.12 Kinetic molecular model

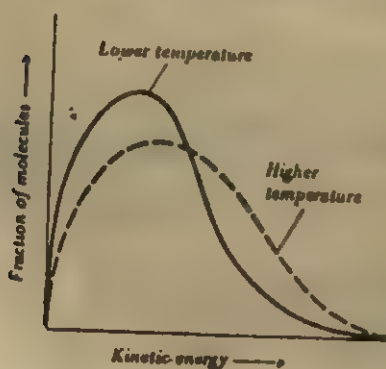


Fig 3.13 Molecular speed distribution at two temperatures

4. The pressure exerted by a gas is the result of the bombardment on the container walls by the molecules.
5. The molecules are so small that their volume is negligible as compared to the total volume of the gas. Thus the gas occupies the total space available to it.
6. There is no force of attraction among the molecules of a gas.
7. The motion of these molecules is not effected by gravitational force.
8. The average kinetic energy of the gas molecules is propotional to the temperature of the gas.

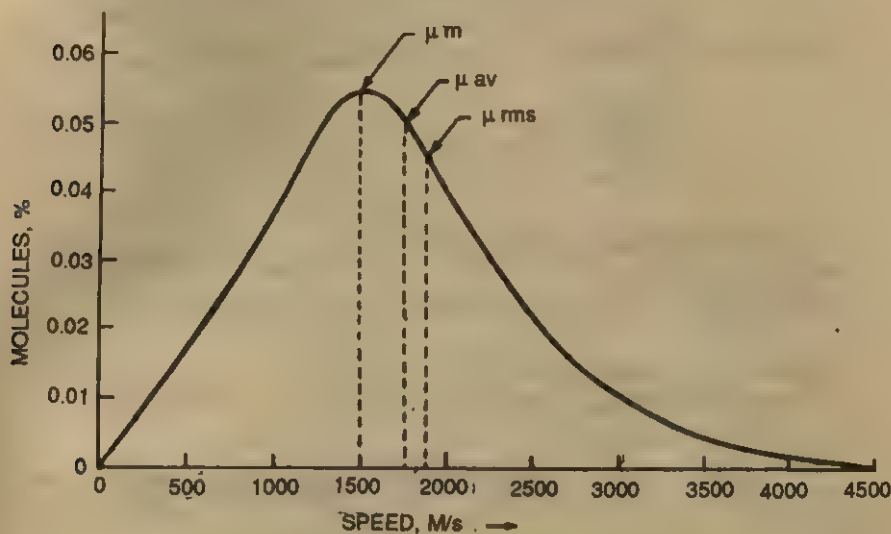


Fig. 3.14 A distribution of molecular speeds

3.6.1 Kinetic Gas Equation

It is being assumed that the pressure exerted by a gas is due to the collision of its particles with the walls of the container and as there is no preferential direction to this motion. The gas molecules would collide with all the walls of the container with the same ease and hence would exert uniform pressure in all the directions.

Let n be the number of molecules, each having a mass, m , moving with a root mean square velocity, C , exert a pressure P , when enclosed in a container of volume V . The pressure of the gas can be calculated and an equation is obtained. This equation 3.32 is known as the kinetic gas equation

$$PV = \frac{1}{3} mnC^2 \quad (3.32)$$

3.6.2 The Relation Between Average Kinetic Energy And Absolute Temperature

The Kinetic gas equation is

$$PV = \frac{1}{3} mnC^2 = \frac{2}{3} \times \frac{1}{2} mnC^2$$

In one mole of any gas, the number of molecules = N (The Avogadro's Number)

For one mole of a gas

$$PV = \frac{2}{3} \times \frac{1}{2} mnC^2 = \frac{2}{3} N \times \frac{1}{2} mC^2 \quad (3.33)$$

Also, for one mole of a gas, the ideal gas equation $PV = nRT$ becomes

$$(3.34)$$

$$PV = RT \quad (3.35)$$

From equation (3.26) and (3.27)

$$RT = \frac{2}{3} N \times \frac{1}{2} mC^2 \quad (3.36)$$

Now $\frac{1}{2} mC^2$ represents the average kinetic energy of one molecule :
(ke)_{av}

$$\text{Therefore,} \quad T = \frac{2}{3} \frac{N}{R} \times (\text{ke})_{\text{av}} \quad (3.37)$$

Here N and R are constants

Therefore, from equation (3.37)

$$T = \text{A constant} \times (\text{ke})_{\text{av}}$$

or the temperature of a gas is proportional to the average kinetic energy of its molecules.

3.6.3 Boyle's Law From The Kinetic Gas Equation

The kinetic equation may be rearranged as

$$PV = \frac{1}{3} mnC^2 = \frac{2}{3} n \times \frac{1}{2} mC^2$$

Examining the right hand side of the equation we find $\frac{2}{3}$ is a constant, n , the number of molecules in a fixed quantity of a gas is also constant and $\frac{1}{2} mC^2$, the average kinetic energy of one molecule at a fixed temperature too is constant. (Why ? Because $\frac{1}{2} mC^2$ is proportional to temperature, T .)

Hence for a fixed mass of a gas at constant temperature, the right hand side of the equation is a product of three constants, viz. $\frac{2}{3}$, n and $\frac{1}{2} mC^2$

The product of the three constants will also be a constant.

$$PV = \text{a constant.}$$

Thus, when the gas mass and its temperature have a fixed value,

$$P \propto \frac{1}{V} \text{ which is Boyle's law.}$$

3.6.4 Charles-Gay Lussac Law From Kinetic Gas Equation

According to kinetic gas equation

$$PV = \frac{1}{3} mnC^2 = \frac{2}{3} n \times \frac{1}{2} mC^2$$

For a fixed quantity of a gas n is a constant

(ke)_{av} = $\frac{1}{2} mC^2$, is proportional to T

or $\frac{1}{2} mC^2 = AT$ (where A is constant)

Substituting the values in the kinetic gas equation we get

$$PV = \frac{2}{3} n AT$$

Thus, for a fixed mass of a gas (constant = $\frac{2}{3} nA$)

$$PV = \text{a constant} \times T$$

Thus, in a fixed mass of a gas,

$$V \propto T \text{ (when pressure is kept constant)}$$

This is a mathematical form of Charles law. Also $P \propto T$ (when volume of a given mass of a gas is kept constant) is Gay Lussac law.

3.6.5 Avogadro's Law From Kinetic Gas Equation

For two different gases, the kinetic equations may be written as

$$P_1 V_1 = \frac{1}{3} m_1 n_1 C_1^2$$

$$= \frac{2}{3} n_1 \times \frac{1}{2} m_1 C_1^2 \text{ (For gas I).....(3.38)}$$

$$\text{and } P_2 V_2 = \frac{1}{3} m_2 n_2 C_2^2$$

$$= \frac{2}{3} n_2 \times \frac{1}{2} m_2 C_2^2 \text{ (For gas II).....(3.39)}$$

If $P_1 = P_2$, and $V_1 = V_2$

in such a case from the equations (3.38) and (3.39) we get

$$\frac{2}{3} n_1 \times \frac{1}{2} m_1 C_1^2 = \frac{2}{3} n_2 \times \frac{1}{2} m_2 C_2^2 \text{.....(3.40)}$$

When the two gases are at the same temperature the average kinetic energy of one molecule of gas I = average kinetic energy of one molecule of gas II

$$\text{or } \frac{1}{2} m_1 C_1^2 = \frac{1}{2} m_2 C_2^2 \text{.....(3.41)}$$

Dividing equation (3.40) by equation (3.41)

$$\frac{2}{3} n_1 = \frac{2}{3} n_2 \text{.....(3.42) or } n_1 = n_2 \text{.....(3.43)}$$

Thus at the same temperature and pressure equal volumes of the gases I and II (any two gases) contain equal numbers of molecules.

This is in accordance with Avogadro's law.

3.6.6 Graham's Law Of Gaseous Effusion From Kinetic Gas Equation

At the same temperature, the average molecular kinetic energies of all the gases are the same. For two different gases, therefore,

$$\frac{1}{2} m_1 C_1^2 = \frac{1}{2} m_2 C_2^2 = A \text{ (where A is a constant)}$$

$$\text{or } \frac{C_1^2}{C_2^2} = \frac{m_2}{m_1}$$

$$\text{or } \frac{C_1}{C_2} = \sqrt{\frac{m_2}{m_1}} \dots \dots \dots (3.44)$$

Since the rates of effusion r_1 and r_2 of the gases at a fixed temperature and under same pressure gradient are directly proportional to the average velocities which, in turn, are proportional to root mean square velocities of their molecules,

$$\frac{r_1}{r_2} = \frac{C_1}{C_2} \dots \dots \dots (3.45)$$

From (3.44) and (3.45) we have

$$\frac{r_1}{r_2} = \sqrt{\frac{m_2}{m_1}}$$

$$\text{But } \frac{\text{Molecular mass of Gas II}}{\text{Molecular mass of Gas I}} = \frac{\text{Vapour density of gas II}}{\text{Vapour density of gas I}}$$

$$\text{or } \frac{m_2}{m_1} = \frac{d_2}{d_1}$$

$$\frac{r_1}{r_2} = \sqrt{\frac{m_2}{m_1}} = \sqrt{\frac{d_2}{d_1}}$$

This is Graham's law of effusion.

3.6.7 Dalton's Law of Partial Pressures

For a gaseous mixture of many gases, the total kinetic energy is
 $(K.E)_1 + (K.E)_2 + (K.E)_3 + \dots \dots \dots (K.E)_n \dots \dots \dots (3.46)$

For any gas, according to the kinetic equation

$$\begin{aligned} PV &= \frac{1}{3} m n C^2 \\ &= \frac{2}{3} \left[\left(\frac{1}{2} m C^2 \right) \times n \right] \\ &= \frac{2}{3} \times (K.E) \end{aligned}$$

$$\text{or } (K.E) = \frac{3}{2} PV$$

In general, Kinetic energy = $\frac{3}{2} \times$ pressure of the X its volume. Since all the gases in the mixture are in the same vessel having volume, V , substituting $\frac{3}{2}PV$ for (K.E.) 's of various gases is equation (3.46).

$$(K.E.)_{\text{total}} = \frac{3}{2} P_1 V + \frac{3}{2} P_2 V + \frac{3}{2} P_3 V + \dots + \frac{3}{2} P_n V \dots (3.47)$$

Where P_1, P_2, P_3, \dots are the partial pressures of individual gases.

$$(K.E.)_{\text{total}} = \frac{3}{2} P_{\text{total}} \times V \dots (3.48)$$

From equation (3.47) and equation (3.48) we have

$$\frac{3}{2} P_{\text{total}} \times V = \frac{3}{2} P_1 V + \frac{3}{2} P_2 V + \frac{3}{2} P_3 V + \dots + \frac{3}{2} P_n V$$

$$\text{or } P_{\text{total}} = P_1 + P_2 + P_3 + \dots + P_n$$

which is a mathematical form of Dalton's law of partial pressures.

From the above discussion it is seen that the fundamental kinetic equation can be used as the basis for deriving all the gas laws. The gas laws are nothing but statements of facts about the gases. It is, therefore, clear that the kinetic theory of gases can explain the experimentally observed facts about gases. Broadly speaking the theory seems to be quite sound.

3.7 KINETIC ENERGY OF AN IDEAL GAS

Energy by virtue of motion of a body is called the kinetic energy of the body. The molecules in a gas are in constant motion. The kinetic energy of a gas as a whole can be obtained by adding together the kinetic energies of its molecules. According to kinetic gas equation.

$$PV = \frac{1}{3} mnC^2$$

3

and according to ideal gas equation

$$PV = nRT$$

Grouping above equations, we get

$$\frac{1}{3} mnC^2 = nRT$$

$$\text{or } \frac{2}{3} \times \frac{1}{2} mC^2 \times n = nRT$$

$$\text{Since } \frac{1}{2} mC^2 = (K.E.)_{\text{av}} \text{ (By definition)}$$

n = number of molecules in the gas

$$\therefore \frac{1}{2} mC^2 \times n = (K.E.)_{\text{total}}$$

From above equations

$$\frac{2}{3} \times (\text{total kinetic energy}) = nRT$$

Therefore, total Kinetic energy for n moles of an ideal gas

$$= \frac{3}{2} nRT \dots \dots (3.49)$$

For one mole (K.E) total $= \frac{3}{2} RT$

Exercise 3.11 Assuming methane to be an ideal gas calculate the average kinetic energy of two moles of methane at 127°C .

Here $n = 2$ moles $R = 8.314$, joules (deg. Kelvin) $^{-1} \text{ mol}^{-1}$

$$T = 127 + 273 = 400^\circ\text{K}.$$

Substituting the values in the equation (3.49) we get

$$\text{K.E.} = \frac{3}{2} \times 2 \times 8.314 \times 400$$

$$= 9976.8 \text{ joules}$$

3.8 CALCULATIONS OF MOLECULAR VELOCITIES

From the kinetic gas equation

$$PV = \frac{1}{3} mnC^2$$

In one mole of any gas $n = N$, the Avogadro's number

For one mole of a gas

$$\begin{aligned} PV &= \frac{1}{3} mNC^2 \\ &= \frac{1}{3} MC^2 \end{aligned}$$

Where $M = mN$, the gram molecular mass and V is the volume per mole.

$$\text{or } C^2 = \frac{3PV}{M}$$

$$\text{or } C = \sqrt{\frac{3PV}{M}} \dots \dots \dots (3.50)$$

Since $\frac{M}{V} = d$, the density of the gas

$$\text{Therefore, } C^2 = \frac{3P}{d} \dots \dots \dots (3.51)$$

Also since for one mole of a gas

$$PV = RT$$

Equation (3.50) can be written as

$$C = \sqrt{\frac{3RT}{M}} \dots \dots \dots (3.52)$$

$$= \sqrt{\frac{3 \times 8.314 \times 10^7 \times T}{M}} = 1.58 \times 10^4 \sqrt{T/M} \text{ Cm s}^{-1} \dots \dots (3.53)$$

real gases deviate from ideal behaviour.

3.9.1 Deviations Of Real Gases From Gas Laws

(i) **Deviations from Boyle's law :** According to Boyle's law, the product of pressure and volume for a given mass of a gas, at a constant temperature should remain constant. In the Table 3-2 the actual values of PV for hydrogen, nitrogen and carbon dioxide are given. It is seen from this table that the PV values vary quite significantly. It is also seen from the table -

- (i) that values of PV increase continuously with increase of pressure for hydrogen.
- (ii) that in case of nitrogen and carbon dioxide, values of PV first decrease and then increase.
- (iii) that the deviations at high pressures are more pronounced.

TABLE 3.2

Pressure atm	Values of PV for different gases		
	H_2 at $0^\circ C$	N_2 at $0^\circ C$	CO_2 at $40^\circ C$
1	1.000	1.000	1.000
50	1.031	0.985	0.741
100	1.064	0.985	0.270
200	1.134	1.037	0.409
400	1.277	1.256	0.718
800	1.566	1.796	1.299

(ii) **Deviations from Charles-Gay Lussac Law:** According to this law the volume of a given mass of a gas at constant pressure should vary directly with temperature on the Kelvin scale. The shapes of PV versus P curves at various

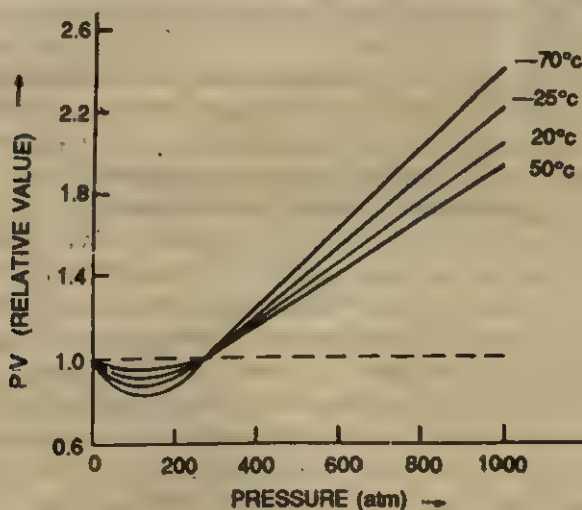


Fig. 3.15 Pressure - volume product as a function of pressure for nitrogen at different temperatures

temperatures should be the same. However, on plotting PV versus P for nitrogen at various temperatures (based on experimental data of the kind shown in column 3 of the Table 3.2) we get curves shown in Fig. 3.15

It is seen that the shapes of curve change with the change in temperature. Thus, Charles-Gay Lussac law also is not obeyed by the real gases at all temperatures and pressures. The following important points may be noted from the curves in Fig. 3.15

(i) The departure from the law is more pronounced at high pressures.

(ii) Considerable deviations occur as the temperature is lowered.

These become greatly pronounced as the temperature approaches the liquefaction point (-183°C for N_2)

(iii) Deviations from Avogadro's law : In the Table 3.3 below are given the actual volumes occupied by one mole of gases at STP.

TABLE 3.3

Gas	Volume occupied by one mole at STP
Hydrogen	22.427 litres
Oxygen	22.394 litres
Nitrogen	22.405 litres
Carbon dioxide	22.264 litres
Ammonia	22.084 litres
Ethyl chloride	21.879 litres

If the law were strictly true, these volumes would have been independent of the nature of the gas. The results in the Table 3.3 show that this is not the case.

In general, it may be pointed out that deviations from the gas laws are not very significant when the pressure is of the order of one atmosphere and the temperature is not near the liquefaction point. Lower the pressure and higher the temperature, more ideally do the gases behave.

3.9.2 The Causes of Deviations From Ideal Gas Laws

The Kinetic theory of gases was propounded to find a common basis for the gas laws. The postulates of the theory, when translated to a mathematical equation, gave the relation $PV = \frac{1}{3} mn C^2$. It was shown earlier that the ideal gas laws could be derived from this relation. A closer examination of the data collected at various temperatures and pressures has revealed to us that real gases show deviations from the laws and these deviations are more pronounced at lower temperatures, higher pressures and with more easily liquifiable gases. It implies that the kinetic theory of gases which holds strictly for an ideal gas, fails to explain the behaviour of real gases. In

- (i) There is something wrong with the postulated model for the gases, i.e., one or more postulates of the theory may be wrong.
- (ii) The mathematical treatment is not exact.

Let us have another look at the gas model. Two of the postulates of the kinetic theory are:-

- (i) The volume of the molecules of the gas is negligible in comparison with the total space occupied by the gas.
- (ii) The molecules do not exert any force upon one another.

In reality neither of the two postulates can be regarded as sound when applied to real gases. Let us see how it is so

(a) **Gas molecules do have volume :** As material bodies gas molecules do have volumes which, of course, is quite small as compared to the space occupied by the gas (at high temperatures and low pressures).

On increasing the pressure and/or decreasing the temperature the volume of the gas is reduced. What may be regarded as negligible volume for gas molecules, when the space volume is large, will not remain negligible when the space volume is made small by compressing the gas, (you can neglect the volume of the chalk pieces in a lecture room but cannot do so in relation to the chalk holder attached to the black-board). The total volume of the molecules in a gas will probably be of the same order as the volume of the solidified gas.

(b) **The intermolecular forces of attraction come into play :**

The fact, that gases can be converted into liquids, shows that some kind of intermolecular force exists in gases. An experimental evidence to the existence of the attractive force in gases was obtained by Joule and Thomson. They passed a stream of gas at constant pressure through a tube into which a porous plug was fixed. In general, the gas coming out of the plug was found to be cooler than the gas on its other side. This occurred because the gas expanded in passing through the porous plug in a lower pressure region and for this energy would be required if any force of attraction existed between the molecules.

These observations lead us to believe that at least the postulates of the kinetic theory of gases listed above do not hold good for real gases.

3.9.3 Van der Waal's Equation

Considering the existence of intermolecular forces in gases and making an allowance for the volume of the molecules of gases. J.D. van der Waals made an attempt to develop a simple equation of state for real gases. He applied appropriate volume and pressure corrections in the equation for one mole of an ideal gas and gave the equation.

$$\frac{(P+a)(V-b)}{V^2} = RT \dots \dots \dots (3.54)$$

3.10 THE SOLID STATE AND ITS CHARACTERISTICS

In the solid state of matter, the particles are very closely placed and occupy more or less definite positions relative to one another. Hence, they possess small kinetic energy. The interparticle forces of attractions are very strong in solids.

Thus, solids are rigid bodies and possess definite shape and volume. The molecules in solids are arranged in a definite order and move in a periodic motion but about their mean positions. This does not allow the solids to change their shape. However, it is possible for molecules to escape from the crystal or solid form. There is a very little empty space in solids. The average distance between the neighbouring particles is comparable to the size of the molecules themselves. Crystals possess geometric shapes which are characterized by plane surfaces intersecting at fixed angles. The forces within a solid are strong enough to overcome a considerable external stress.

The rigidity of solids varies too much. Under great stress, a solid may crumble (brittleness) or spread out to a thin sheet (malleability or ductility). On removing stress it may return to its original shape (elasticity). Conduction is another important property of solids. Solids conduct heat and electricity to a varying degree. This difference is attributed to the radically different forces in solids arising from interparticle behaviour.

In solids, we deal primarily with the crystalline state. In our laboratories we see various types of crystals right from colourless sodium chloride to highly coloured potassium permanganate. A crystalline solid is characterized mainly by three characteristics:

1. A definite melting point
2. A definite heat of fusion
3. A definite crystal lattice

Apart from being in a crystalline state, solids may be of an amorphous type (Fig. 3.16). These are also rigid bodies but do not conform to the three characteristics of crystalline solids. Glass, rubber, fused silica, tar, solid glue, helical sulphur and many organic polymers fail to acquire the degree of order, typical of a crystal lattice. They have no definite melting points (soften over an appreciable temperature range) and definite heat of fusion. The order of structural units does not prevail over long distance. Amorphous solids also occupy definite volume and maintain a definite shape. There are substances which in their powdered form appear to be amorphous, but microscopic examination reveals their crystalline nature. At times amorphous solids possess both crystalline and noncrystalline characteristics. A crystalline solid, when cut with a sharp edged knife gives a clean and regular cleavage but an amorphous substance gives an irregular or conchoidal fracture (Fig. 3.17).

Glass, a typical and common amorphous solid, is not a specific chemical substance because of wide variations in the composition of various types of glasses. Its rigidity, hardness and resistance to shear have not been

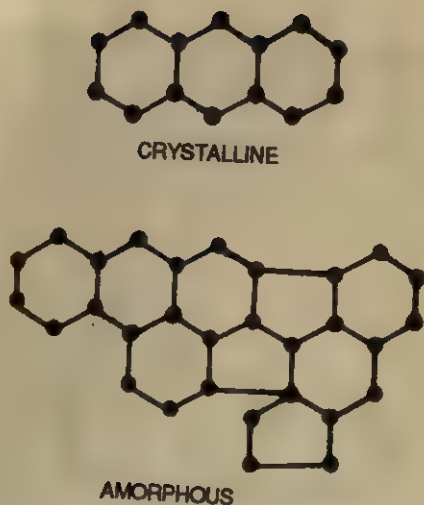


Fig. 3.16 A crystalline solid and an amorphous solid

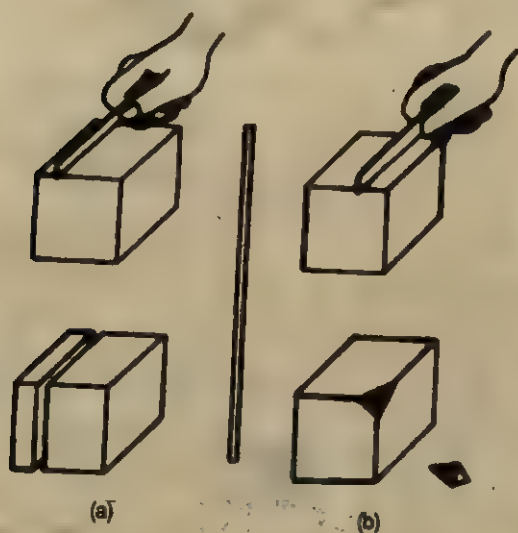


Fig. 3.17 The cutting of solids with knife.
 (a) A clean cut of the plane in a crystalline solid.
 (b) An irregular cut of the plane in an amorphous solid.

types of glasses. Its rigidity, hardness and resistance to shear have not been explained so far. The tendency of glass to flow is indicated by the fact that glasses in windows grow thick at the bottom and become thin near the top over a long time. Another common amorphous solid is sulphur. On quenching molten sulphur (S_8) at room temperature, an open helix (Fig. 3.15) amorphous form is obtained. Over a long period, it reverts to rhombic crystalline form of sulphur.

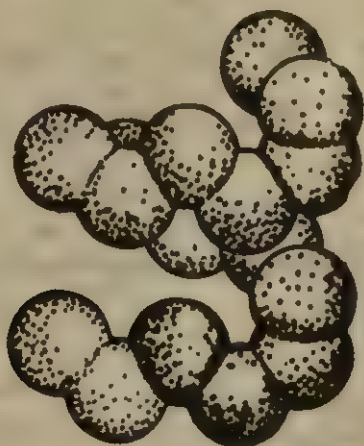


Fig. 3.18 Amorphous sulphur helix

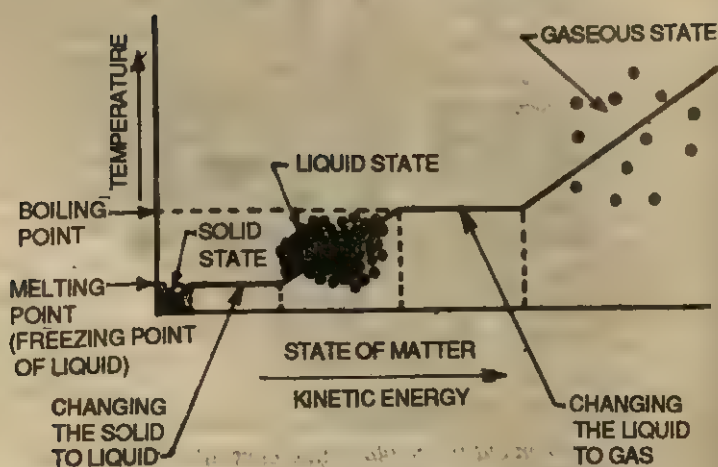


Fig. 3.19 The effect of temperature on a solid

Let us consider what happens when a crystal is heated. The addition of heat energy to a substance raises its temperature. When the temperature of a crystalline solid is raised, its kinetic energy increases. As a result, the atoms, ions or molecules constituting the solid, start vibrating or oscillating violently. Finally a temperature is attained when the crystalline lattice is destroyed by these vibrations. Thus, particles find additional space for movement. The solid gets converted to the liquid state. This process is called melting. (Fig. 3.19) Now on cooling the liquid state a solid is formed. In solidification process, the kinetic motion of particles decreases and the attractive forces become pronounced. As the temperature is decreased a point is reached at which the particles begin to occupy relatively fixed positions in space. Eventually the particles become arranged in a definite three dimensional pattern in which they occupy definite spatial positions. This process is called freezing (or solidification or crystallization).

From the melting point of a substance, one can decide about the nature of bonding involved (covalent, ionic or metallic) to a good degree of approximation. Ionic solids like NaCl (m.p. 1077K), MgCl_2 (m.p. 1260K), K_2CO_3 (m.p. 1173K), etc, melt at high temperatures because of strong attractive forces within the ions. On the other hand, solids with weaker attractive forces have low melting point, *e.g.*, neon melts at 24K, fluorine at 54K, oxygen at 55K and nitrogen at 63K.

3.11 THE CRYSTAL LATTICE (OR SPACE LATTICE)

Solids tend to crystallize in definite geometric forms. The regular geometric pattern of the units (pattern of points) constituting a crystalline solid is called crystal lattice (space lattice) or simply a crystal. A lattice is a regular three dimensional arrangement of particles occupying relatively fixed positions in space. The positions which the particles occupy in the crystal lattice are lattice sites. The particles occupying lattice sites are held in a definite arrangement by the strong interparticle attractive forces. These particles vibrate about their mean positions (Fig. 3.20), and thus, distribute kinetic energy throughout the solid.

The nature of the particles occupying the lattice sites depends on the nature of the solid. These particles can be atoms, ions or molecules, and hence, they may be described in terms of lattice points. For the lattice points to be equivalent, they must have the same chemical environment. In Fig. 3.21 the three dimensional crystal lattice of sodium chloride is shown. Each Na^+ ion is surrounded by 6 chloride ions and vice versa. Thus, both Na^+ and Cl^- ions have identical environments but are different for the two ions. Therefore, in NaCl the lattice points may be labelled at the sites of either Na^+ or Cl^- ions but not at both.

Further, the particles arrange themselves as warranted by the attractive

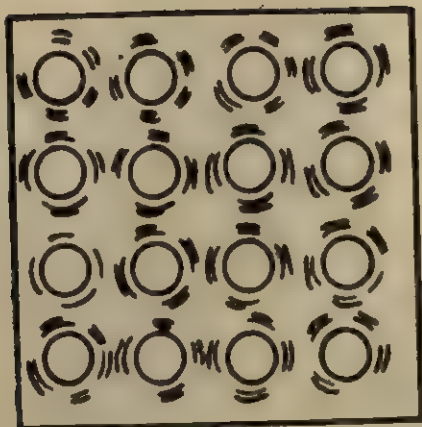


Fig.3.20 The particles in a crystal lattice vibrate about their mean positions.

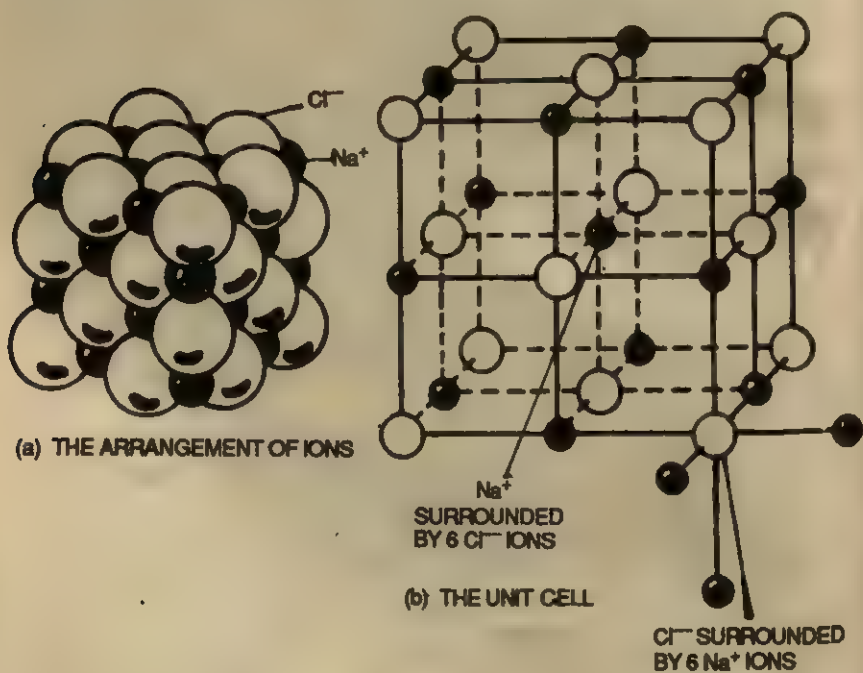


Fig. 3.21 Extended ionic crystal structure of NaCl.

forces. These attractive forces may be electrostatic (interionic), covalent (interionic) or intermolecular forces.

In some solids, the particles arrange themselves in two dimensional covalent networks. The best known example is the graphite structure.

3.12 TYPES OF SOLIDS

Solids are classified on the basis of structural units ions, atoms or molecules and the nature of forces holding particles together in a crystal as follows:

- (i) **Ionic solids** : They are made up of oppositely charged ions which are held by strong electrostatic forces. The mode of packing of ions depends on the relative sizes of positive and negative ions.
- (ii) **Molecular Solids** : Molecular solids essentially consist of neutral molecules held together by relatively weak dipole-dipole or vander Waal's forces. Such solids are of two types, i.e., polar and non-polar. Polar molecules constituting crystal lattice are held by dipole-dipole attraction (Unit -6). The arrangement of the polar molecules depends upon the shapes of the molecules and the strength of attractions. Non-polar molecules are held by vander Waals attractive forces within the crystal lattice. These (Fig 13.22) forces are relatively weak.
- (iii) **Covalent Solids** : In these solids, neighbouring atoms are held by covalent bonds. The network of atoms bonded by covalent bonds grow in size, along fixed directions, to form a giant molecule. It is difficult to distinguish individual molecules in this structure.
- (iv) **Metallic Solids** : In these solids metallic atoms are distributed in a regular and definite pattern which depends on the size and electronic configuration of the atoms constituting the solid. The structural units are positive metal ions (same radii) dispersed in electron gas (Unit -6). These units are held strongly by the strong electrostatic forces between positive metal ions and mobile valence electrons. Various types of solids with their characteristics are summarized in Table 3.4.

3.13 X-RAY DIFFRACTION STUDIES

Much study about crystal structure has been possible by the application of X-ray diffraction analysis. Neutron and electron beams have also been used for the purpose.

The phenomenon of diffraction occurs when radiation is passed through a narrow slit or a grating (parallel slits close together). The beam undergoes diffraction and is scattered at definite angles. The diffracted beams set up an interference pattern of light and dark bands. The nature of this pattern is related to wavelengths of the light and the width of the slit or the spacings between the lines on a diffraction grating (magnitude of wavelengths and width of slit or spacing of lines on grating should be of the same order).

Crystals are found to act as diffraction gratings for X-rays as the structural units in crystals are set in planes at close distances in repeating



Fig. 3.22 Molecular solid-solid carbon-dioxide

patterns and the spacings of units in a crystal lattice are of the same order as the wavelength of X-rays. This technique was first developed in 1912 by Von Laue. Figure 3.23 suggests a method of scattering of X-rays from a crystal.

Later in 1913 W.L. Bragg and his father W.H. Bragg used the technique of X-ray diffraction for the determination of crystal structures. The principle used by them is embodied in the Bragg's equation which correlates the angle of diffraction to the distance between successive planes of structural units (atoms, ions or molecules) in the crystal

$$n\lambda = 2d \sin \theta$$

where

θ = the angle between the X-ray beam and the plane of atoms.

λ = the wavelength of X-rays

d = the distance between successive planes

n = an integer (1, 2, 3,) known as the order number of the diffracted beam

Figure 3.24 pictures two rays a and b, in a monochromatic X-ray beam. Waves a and b are reflected from two successive planes of atoms or ions in a crystal. Wave b travels a little longer distance than a does. If the distance travelled by a is L then b will travel $L + AB + BC$. This additional distance, i.e., $AB + BC$ is equivalent to $2d \sin \theta$ ($\because AB = d \sin \theta$ and $BC = d \sin \theta$). Now if $2d \sin \theta$ is an integral multiple of wavelengths, the rays will be in phase and produce a dark spot on a photographic plate. The interplanar distance can, thus, be determined by knowing λ and θ . As there are differently oriented planes in the crystal, the X-ray beam is broken up into a large number of diffracted beams. From relative intensities of the various

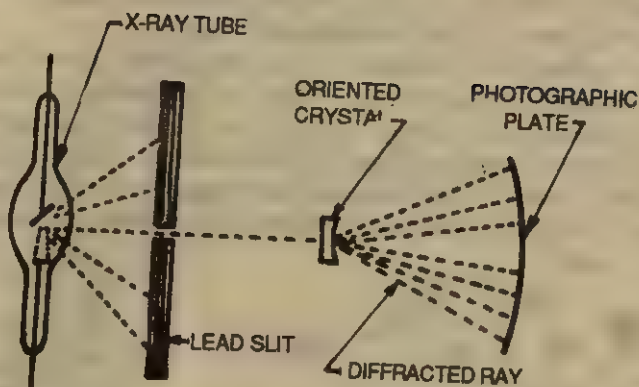


Fig. 3.23 A simple set up for Xray diffraction from a single crystal.

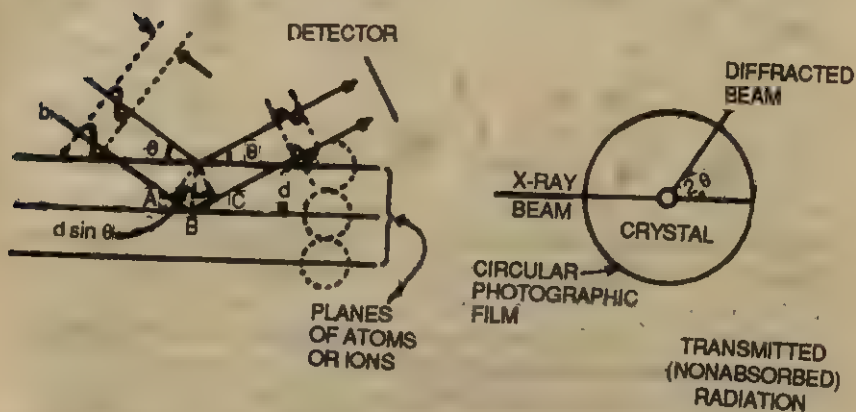


Fig. 3.24 Illustration of Bragg's law of diffraction

beams, the crystalline structure of a solid can be determined. Further, different orientations of the crystal make the studies possible in different directions to arrive at a complete structure of a crystalline solid. Several X-ray diffraction methods have been used. We shall discuss briefly the methods developed by (1) Laue and (2) Debye, Scherrer and Hull.

(1) **Laue's Method** : A polychromatic beam of X-rays was passed through a crystal (say NaCl). A circular pattern of dark spots (Fig. 3.21) was obtained as a result of diffraction satisfying the Bragg's equation. Imperfection and symmetry in crystals can be known by this method.

(2) **Powder Method** : This method was developed by Debye, Scherrer and Hull. A powdered sample of crystalline solid contains small crystals at many random orientations. A monochromatic beam of on a cylindrical film surrounding the sample. A diffraction pattern obtained is shown in Fig. 3.26.

This method is generally used for identification of unknown substances or mixtures by comparison of the powder pattern with patterns of known materials.

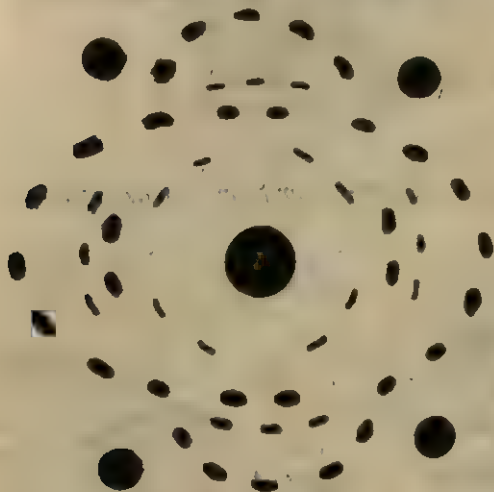


Fig. 3.25 Laue's X-ray photograph for crystalline NaCl



Fig. 3.26 Powder diffraction pattern.

Exercise 3.14. The following observations were made in the first order X-ray diffraction studies of a crystal:

diffraction angle $2\theta = 20^\circ$

interplanar distance = 0.4 nm. Calculate the wavelength of the X-ray used.

Solution : According to Bragg's equation,

$$\begin{aligned} n\lambda &= 2d \sin n = 1 \\ &= 2 \times 0.4 \times 10^{-9} \text{ m} \times \sin 10^\circ \\ &= 2 \times 0.4 \times 10^{-9} \text{ m} \times 0.1736 \\ &= 0.13888 \text{ nm} \\ &= 1.3888 \text{ \AA} \end{aligned}$$

3.14 CRYSTAL LATTICES (SYSTEMS) AND UNIT CELLS:

A crystal lattice (or space lattice) is a general term for an arrangement

of points in space representing the atoms, ions or molecules forming the crystal which if extended in all directions throughout the crystal forms a repeating unit giving a shape of the crystal.

A unit cell is the closely defined entity consisting of minimum portion of crystal lattice with just minimum number * of particles which shows the pattern of the entire lattice. Such units are repeated over and over again in three dimensions and generate the entire crystal. The collection of points in the unit cell indicate the crystal coordination number and are in consistence with the formula of the compound. The unit cell of sodium chloride is shown in Fig. 3.27. It consists of 27 points. It shows the face-centred cubic arrangement of Cl^- with Na^+ ions placed in the interstices or holes.

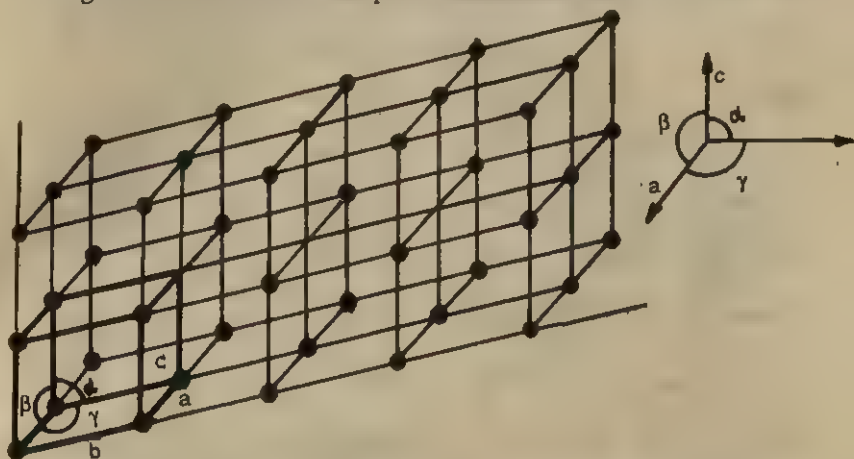


Fig. 3.27 A three dimensional lattice and a unit cell.

A close view of the lattice along a diagonal indicates the alternate planes of Na^+ and Cl^- ions. This valuable information is supplied by X-ray diffraction. Thus, the basic information which is provided by X-ray diffraction concerns with the dimensions and geometric form of what is known as a unit cell.

A unit cell is characterized by the distances, a , b and c along the three edges of the unit cell and the angles α , β and γ between the pairs of edges (b, c), (c, a) and (a, b) respectively. The angles between the axes are 90° , and this is specified by the notation $\alpha = \beta = \gamma = 90^\circ$ and when $a = b = c$, the array is the simple cubic system. The entire crystal can be generated by a stepwise shifting of the (simple translation or displacement in three dimensions) unit cell in three dimensions.

Among the various types of crystals, there are many variations in lattices and unit cells. The number of unit cells depends upon the size of the

* The number of units is such that it is just sufficient to define the repeating unit and also usually sufficient to show the symmetry elements of the crystal.

crystal. If lattice points occupy only the corners of a unit cell in a crystal lattice, the crystal is said to have a simple lattice. There are seven basic crystal systems (Table 3.5) or crystal habits on the basis of seven primitive simple unit cells. A crystal system can be defined in terms of its coordinates. Lines drawn parallel to and of lengths equal to the sides of a unit cell are called lattice coordinates of lengths a, b and c .

The seven crystal systems may be further subdivided into fourteen space lattice types called Bravais lattices. These lattices may be primitive (P), body-centered (B), face-centred (F) or centred on one face or end-centred (E) as portrayed in Fig. 3.28, *e.g.*, crystals with cubic lattice are of three types *i.e.*, simple cubic, face-centred cubic (fcc) and body-centred cubic (bcc) crystals (Fig. 3.28 and Fig. 3.29).

TABLE 3.5 Crystal Systems

System	Lattice type	Axes	Angles	Examples
Cubic	P,F,B	$a=b=c$	$\alpha = \beta = \gamma = 90^\circ$	Rock, salt, zinc blende, Cu, CaCl ₂ , CaO
Tetragonal	P,B	$a=b \neq c$	$\alpha = \beta = 90^\circ$	White tin, SnO ₂ , rutile (TiO ₂)
Orthorhombic	P,B,F,E	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, HgCl ₂ , K ₂ SO ₄ , I ₂
Monoclinic	P,E	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	Monoclinic sulphur, KClO ₃ , FeSO ₄ · 7H ₂ O
Triclinic	P	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	K ₂ Cr ₂ O ₇ , CuSO ₄ · 5H ₂ O
Hexagonal	P	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	Quartz, graphite, ice
Rhombohedral	p	$a=b=c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite, magnesite

P= Primitive, B= Body-centered, F=Face-centred, E= End-centred

All faces of crystals do not grow at a regular rate during crystallization. As a result of this, all crystals of a substance may not assume the same ratio of axial edges as the unit cells but their axial angles are of the identical order. Actual crystals with identical unit cells may differ in their final shapes. In Table 3.6 some crystal structures with their basic habits are given.

3.15 PACKING OF CONSTITUENT PARTICLES IN CRYSTALS:

The minimum number of points which define a unit cell can locate atomic, ionic or molecular centres, *i.e.*, constituent particle centres. In the growth of crystals these constituent particles get closely packed together. These particles pack themselves as efficiently as possible so that the volume is minimum. This state refers to a state of maximum possible density. The constituent particles can be of various shapes, hence, the mode of packing of particles will vary according to their shapes. The structure of many crystals can be related to the close packing of spheres which could be of

different sizes. Ionic crystals structures are particularly complicated by the different sizes and nature (not of the same kind) of structural units. In this section we shall discuss the modes of packing of those crystals which are composed of only one kind of atoms.

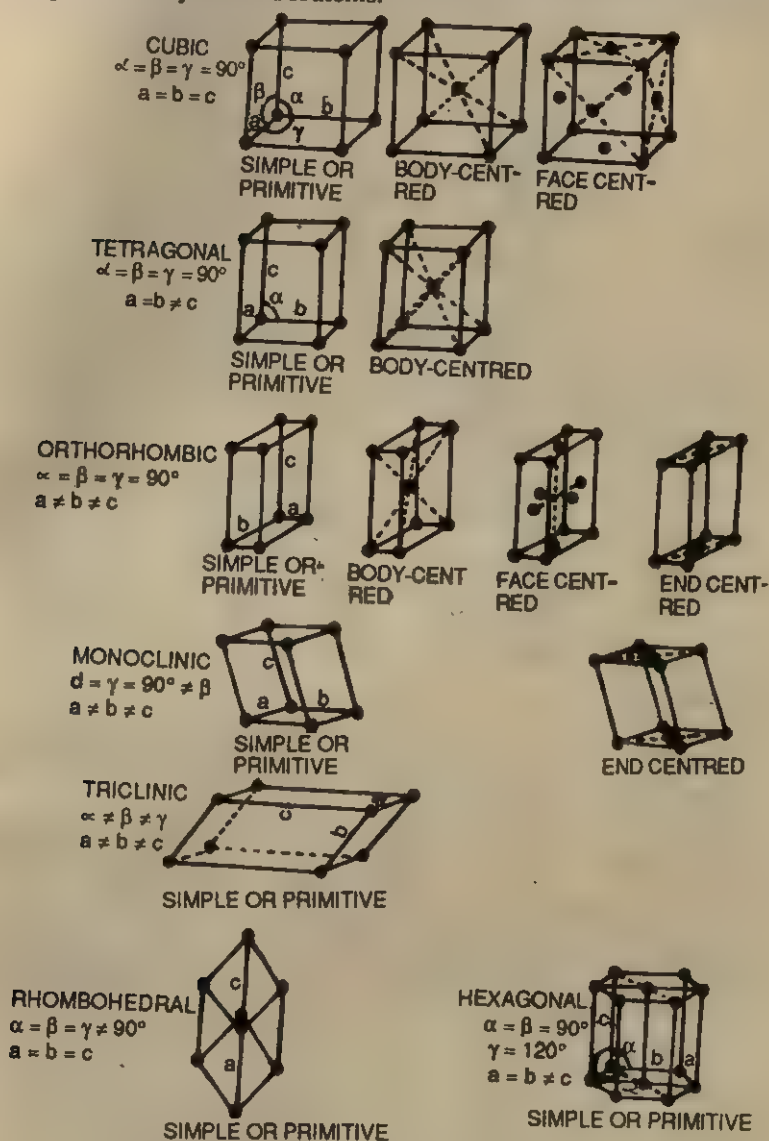


Fig. 3.28 Bravais lattices (crystal systems).

Metallic crystals are the best representatives of crystals containing one kind of atoms. A pure metal crystal contains only one kind of atoms, and so, all the constituent particles in the structure are of the same size. Thus, there

TABLE 3.6 Crystal structures and lattice types

Compound	Lattice type	Compound	Lattice type
NaCl	Cubic (F)	Flourite	Cubic (F)
CsCl	Cubic (B)	Rutile	Tetragonal (B)
Zinc blende	Cubic (F)	Cristobalite	Cubic (F)
Wurtzite	Hexagonal (P)	CdI_2	Hexagonal
NiAs	Hexagonal (P)	Calcite	Rhombohedral
Pyrites	Cubic (F)	Quartz	Hexagonal
Cuprite	Cubic (B)	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Triclinic
Sulphur	Orthorhombic	Sulphur	Monoclinic
Diamond	Cubic (F)	K_2PtCl_6	Cubic (F)

are no complexites arising from packing of particles of different sizes together, as occur with crystals of ionic solids and some other classes of solids. Towards the end of this section, we shall also discuss briefly the packing of particles involved in ionic solids.

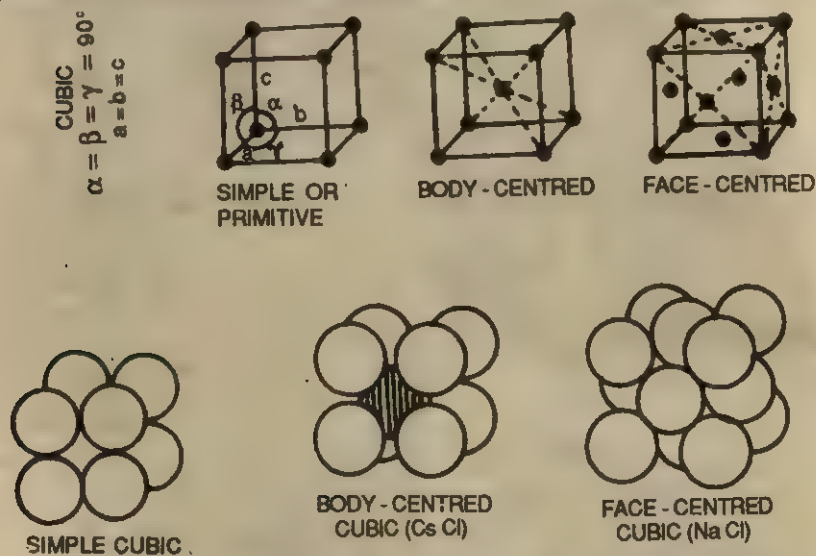


Fig. 3.29 Geometry of packing of ions and the shapes of crystals.

There are several ways in which a number of spheres of equal size can be packed in layers. Some of these are shown in Fig. 3.0 Arrangement of spheres in a row in horizontal alignment relates to the edge (Fig. 3.30(a)) of a crystal. Further addition of rows vertically forms a crystal plane. Thus, Fig. 3.30 (b) and (c) refer to the arrangements of spheres in the first layer (plane formation). In Fig. 3.30 (b) each central sphere is in contact with four other spheres, giving a square close packing. Here the rows are in vertical alignment. In Fig. 3.30 (c) each central sphere is in contact with six other spheres, giving a hexagonal close packing. In this arrangement, the spheres

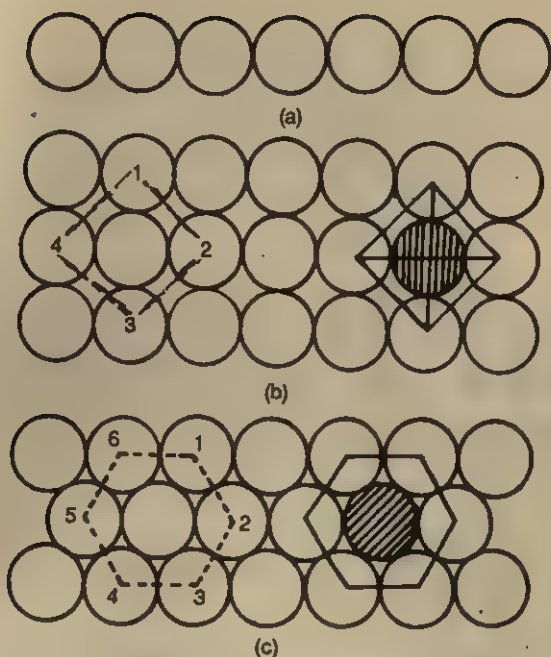


Fig. 3.30 (a) A one dimensional lattice (edge formation), (b) and (c) Two modes of two dimensional lattice (formation of crystal plane).

from alternate rows are placed in the depressions between spheres of the preceding rows, e.g., the spheres from the 2nd row are accommodated in the depressions between spheres of the first row. Thus, the second row is not in vertical alignment of the first row. The spheres in the third row will be vertically aligned with those in the first row and so on. Thus, in the arrangement the available space is used most effectively leaving less space unoccupied than in the arrangement with square close packing. This arrangement is referred to as closed packing of spheres.

Now these two arrangements can be extended further to have a three dimensional lattice. In case of layer exhibiting square close packing, a second similar layer of spheres may be fitted with each sphere either just directly above the spheres or above the holes (or voids or interstices) in the first layer. The first arrangement of superimposition (Fig. 3.31(b) gives simple cubic lattice with successive layers. Thus, each sphere touches six adjacent spheres. Now in the second arrangement (where holes present in the first layer are occupied by the spheres of second layer) when a second layer is fitted with its each sphere on a layer exhibiting square close packing (Fig. 3.31 (c)), a body-centred cubic lattice is generated with addition of successive layers. Every alternate layer has similar arrangement of spheres. Each sphere touches its eight nearest neighbours.

Similarly in the closed packed arrangement, holes (say either L or M)

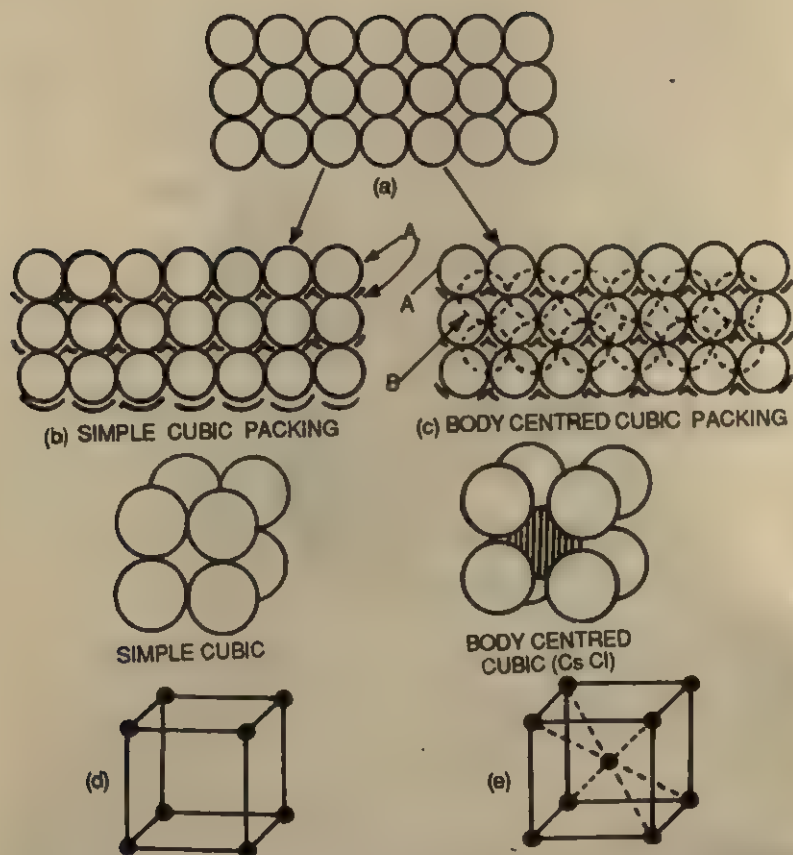
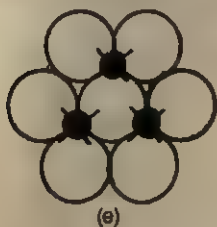


Fig. 3.31 Arrangement of successive layers on a base layer (a) of spheres in a square close packed structure; (b) all successive layers are alike and give simple cubic lattice; (c) every alternate layer is identical and leads to a body centred cubic packing, (d) simple cubic packing with exploded unit cell; (e) body centred cubic packing with exploded unit cell.

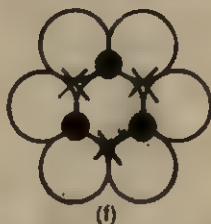
are occupied by the spheres in the second layer. Thus, the second layer is displaced relative to the first layer (Fig. 3.32 (b)). With second layer of spheres, some holes (say M) are left unoccupied, and only, alternate rows of holes are filled. Accordingly there appears to be no other way of filling these unoccupied M holes. There are two alternatives for adding the third layer of spheres upon the second layer. The centres of the spheres in the third layer may be arranged either over the centres of the spheres of the first layer, i.e., spheres in the third layer occupy a row of holes (N) in the second layer corresponding to the centres of spheres present in the first layer (Fig. 3.32 (c)) or they can be displaced so that the centres of the spheres in third layer lie above the holes designated as M in the first layer (Fig. 3.32 (d)). Thus, if A represents the arrangement of spheres in the base layer and B and C represent the different arrangements possible in the successive layers, close

HEXAGONAL CLOSE PACKED

CUBIC CLOSE PACKED

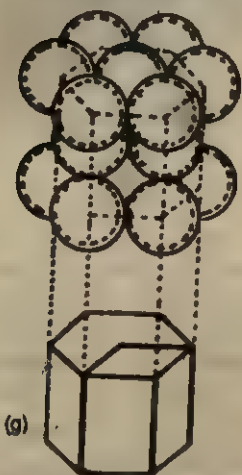


(e)

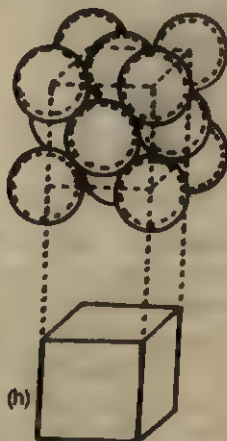


(f)

- ATOMS IN THE PLANE OF THE PAGE
 ○ LOCATION OF CENTRES OF ATOMS IN A PARALLEL PLANE BELOW THE PLANE OF THE PAGE.
 X LOCATION OF CENTRES OF ATOMS IN A PARALLEL PLANE ABOVE THE PLANE OF THE PAGE



(g)



(h)

Fig. 3.32 The two types of close packing; (e) hexagonal close packed, (f) cubic close packed, (g) top view of hexagonal close packing, and (h) top view of cubic close packing.

packed layers can be arranged in the sequence AB, AB..... or ABC, ABC..... .AB, AB..... arrangement is referred to as hexagonal close packing (hcp) [Fig. 3.32 (e) and (g)] and ABC, ABC..... arrangement is referred to as cubic close packing (ccp). [Fig. 3.32 (f) and (h)] The cubic close packed arrangement contains atoms arranged in the face-centred cubic lattice (Fig. 3.33 (d)). The Figs. 3.33 (a) and (c) exhibit the vertical section of hexagonal and cubic close packings. Their exploded unit cells are also shown in Figs. 3.33 (b) and (d).

Holes L and M in the first layer and N in the second layer are all triangular in shape. The hole (say O) in the second layer corresponding to M in the first layer results from the combination of two triangular holes one each from the first and second layers (one triangle vertex upwards and the other triangle vertex downwards). Holes, L, M and N are called tetrahedral

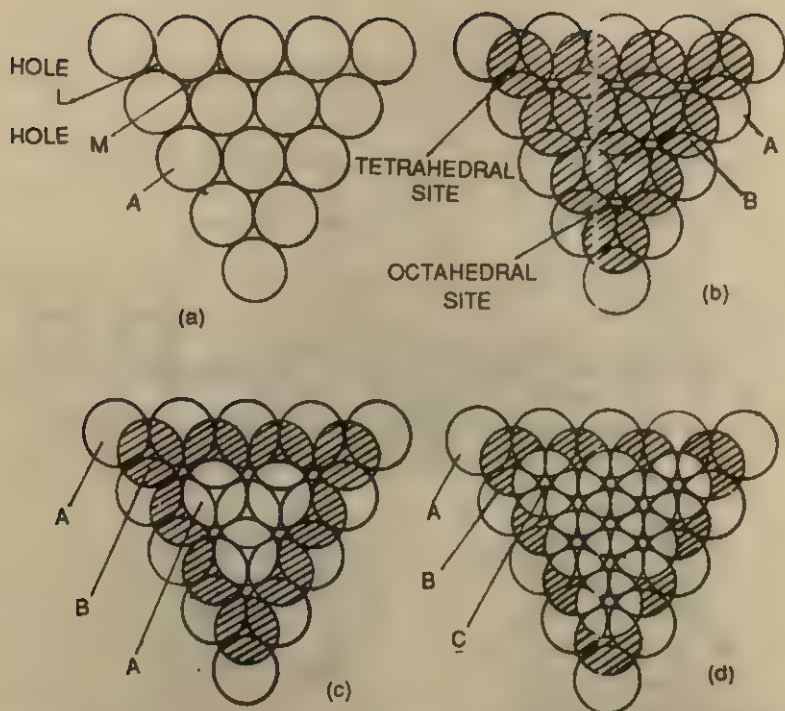


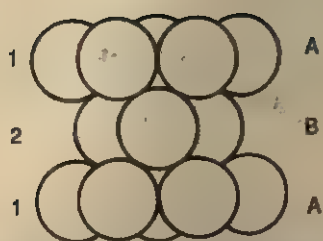
Fig. 3.32 Arrangement of successive layers on a base layer (a) of spheres in a close packed structure; (b) the second layer contains a similar arrangement but the centres of spheres are displaced with respect to the base layer; holes L are occupied but holes M remain unoccupied; (c) the addition of third layer leads to arrangement AB, AB.....which is hexagonal closest packing; (d) the other possible orientation of the third layer leads to arrangement ABC, ABC.....which is cubic closest packing.

holes as they are surrounded by four atoms in a crystal (Fig. 3.34 (a)). Hole O is called an octahedral hole as it is surrounded by six atoms in a crystal (Fig. 3.34(b)). These interstices or holes are quite important particularly in transition elements as the small atoms, such as, H, B, C, N, etc. enter into these interstices forming interstitial compounds.

Both in hcp and ccp structures, each atom is surrounded by twelve other atoms and is said to have coordination number 12 (6 from the base layer and 3 each from the two layers, lying above and below the base layer). In the bcc structure, packing is less efficient and the coordination number is 8.

The major types of structures for the metallic elements are given below:

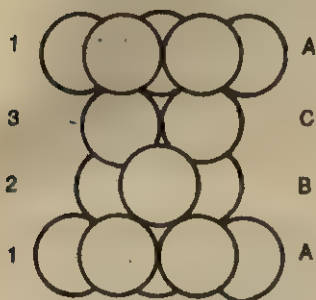
- (a) hcp: Mg, Be, Zn, Ti, Zr, Cd
- (b) ccp: Cu, Ag, Au, Ca, Sr, Al, Ni, Pb, Pt, Co
- (c) bcp: Li, Na, K, Rb, Ba, V, Mo, Cr, W, Fe



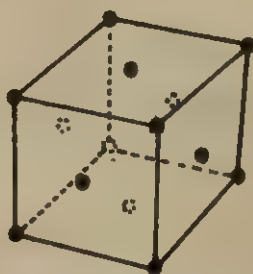
(A) HEXAGONAL CLOSE PACKING OF SPHERES (VERTICAL SECTION)



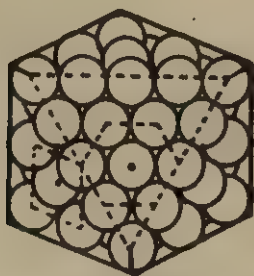
(b) HEXAGONAL CLOSE PACKING OF SPHERES (EXPLODED UNIT CELL)



(c) CUBIC CLOSE PACKING OF SPHERES (VERTICAL SECTION)

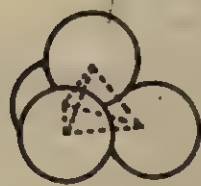
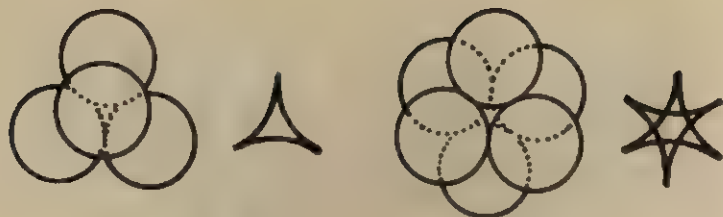


(d) CUBIC CLOSE PACKING OF SPHERES (EXPLODED UNIT CELL EXHIBITING FACE - CENTRED CUBIC NATURE)



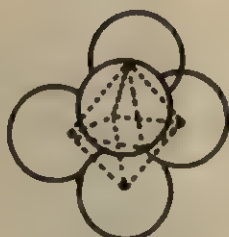
(e) CUBIC CLOSE PACKING OF SPHERES-SHOWING THE CUBIC NATURE

Fig. 3.33 (a) Vertical section of a hexagonal close packing of spheres (b) exploded unit cell of hexagonal close packing of spheres, (c) vertical section of cubic close packing of spheres, (d) exploded unit cell (face-centered cubic nature) of cubic close packing of spheres, and (e) cubic close packing of spheres - showing the cubic nature.



(a)

TETRAHEDRAL HOLE



(b)

OCTAHEDRAL HOLE

Fig. 3.34 Two types of holes exist in the cubic closest packing arrangement of equal sized spheres : (a) tetrahedral hole, and (b) octahedral hole.

Packing in Ionic Crystals

As already said ionic crystal structures are dependent upon the nature of ions and their sizes (anions generally being larger than cations). To understand the lattice, anions are considered as giving a close packed arrangement and the smaller cations fit into the holes among the anions. There are typical five possible close packed arrangements of anions (Fig. 3.35) which depend upon the relative sizes of the cations and anions.

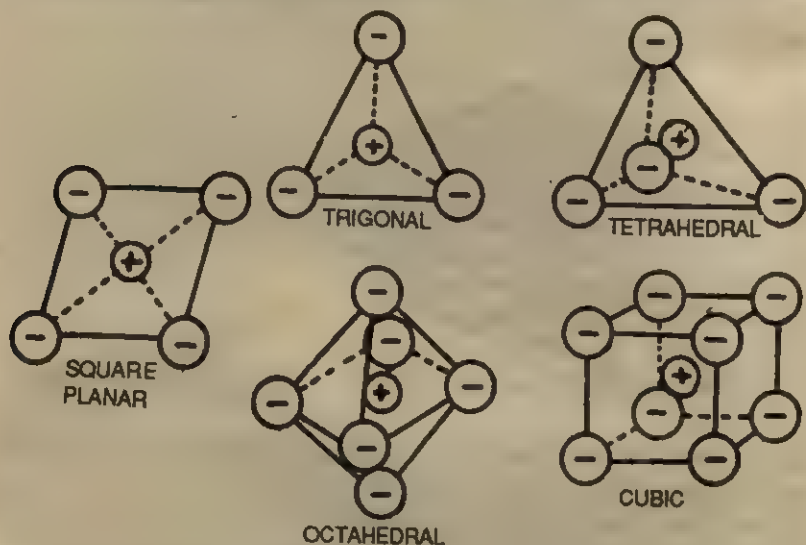


Fig. 3.35 Five close packing

Fig. 3.36 pictures four anions lying in one plane. Two more anions could be accommodated in the hollows (one among the four above and the second among the four below the plane). Now if a matching cation is accommodated into the resulting hole, a satisfactory octahedral packing arrangement of cations and anions will emerge.

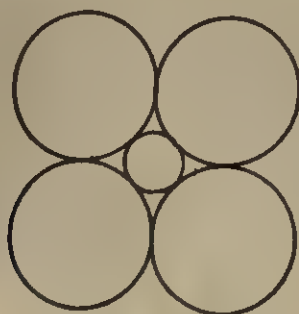


Fig. 3.36 A planar view of octahedral packing of anions around central cation.

There could be other arrangements where either anions are not in contact to one another but cation is touching them or anions are in contact to one another but cation is not touching them.

Table 3.7 lists radius ratio limits for certain types of ionic arrangements with their coordination numbers.

Table 3.7 Relative radius ratios and arrangement of anions.

Crystal coordination number	Anion arrangement	Radius ratio range $r_{\text{cation}}/r_{\text{anion}}$
2	Linear	< 0.15
3	Triangular	$0.15 - 0.22$
4	Tetrahedral	$0.22 - 0.41$
4	Planar	$0.41 - 0.73$
6	Octahedral	$0.41 - 0.73$
8	Cubic	> 0.73

3.16 Properties of Liquids

Volume and shape The intermolecular attractive forces between the molecules in a liquid are strong enough to hold them together and give a

liquid a definite volume. However, the forces of attraction between the molecules are not so strong as to fix the molecules into definite positions. This explains why the liquids do not possess a definite geometrical shape. A liquid flows to fit the shape of its container.

Density and incompressibility. In a liquid the molecules are closer together than the molecules in a gas. That is why the density of a substance in a liquid state is higher than that in a gaseous state. For example, water (liquid H_2O) is 1600 times denser than steam (gaseous H_2O). This also explains the incompressibility of a liquid. The distance between molecules in a liquid is governed by a balance between forces of attraction between molecules and forces of repulsion between neighbouring electron clouds (Fig. 3.37).

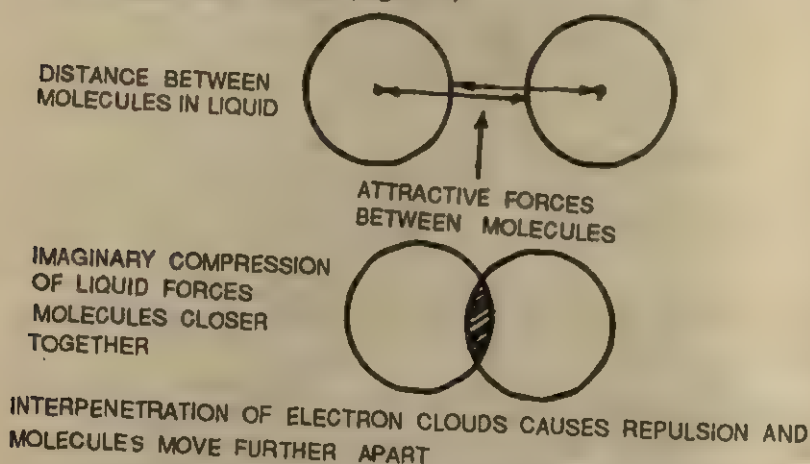
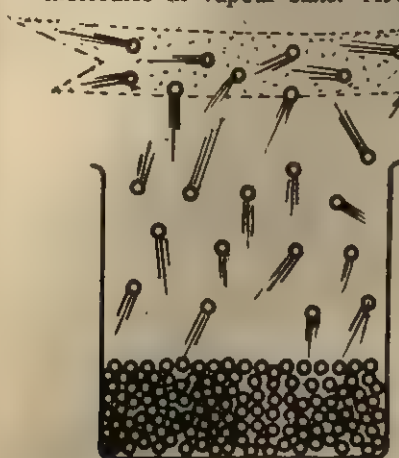


Fig. 3.37. The distance between molecules of a liquid

Diffusion. When two miscible liquids like water and acetone are kept together, they slowly diffuse into each other. The process is much slower compared to that in gases. This is because the movement of molecules is restricted by the attractive forces which bind them into a loose network with neighbouring molecules. At times, a molecule breaks free from the network of molecules that surround it, and moves to another region of the liquid it diffuses.

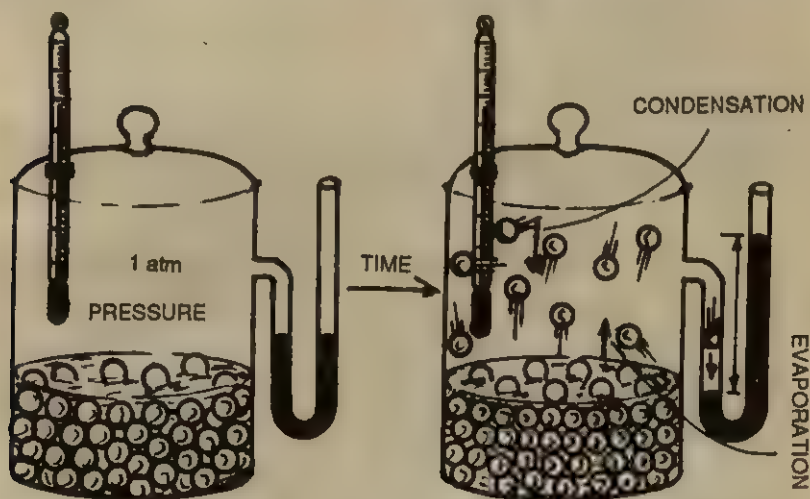
Vapour pressure. Molecules of liquid are in constant motion and thus some of them will have enough kinetic energies to escape from the liquid into the vapour state. When the kinetic energy is sufficient to overcome the attractive forces, molecules pass into the vapour state provided they are near to the surface (Fig. 3.38). This is what happens during the process of the evaporation of a liquid. Considering the evaporation in a closed container at constant temperature (Fig. 3.39), the vapour molecules accumulate in the space above liquid. However the molecules in the vapour state will collide with the walls of the container, and some will be directed back

towards the liquid, some of these will return to the liquid *i.e.* condense (Fig. 3.39). The rate of condensation is proportional to the concentration of molecules in vapour state. At one stage the rate of condensation becomes



equal to the rate of evaporation. This is referred to as the equilibrium state when the liquid level as well as the concentration of molecules in the vapour state become constant. The pressure of the vapours in equilibrium with the liquid, at any given temperature, is called the vapour pressure of the liquid. It is a characteristic property of a liquid. With an increase in the temperature of a liquid, its vapour pressure also increases (Fig. 3.40) because at a higher temperature the liquid contains more molecules having sufficient kinetic energy (Fig. 3.49) to overcome intermolecular attractive forces.

Fig. 3.38. Evaporation of liquid from an open vessel



(a) INITIAL : LIQUID ONLY

(b) EQUILIBRIUM : LIQUID AND VAPOUR
RATE OF EVAPORATION = RATE OF CONDENSATION

Fig. 3.39 (a) The space above the liquid is occupied by air only.

(b) As time passes, liquid evaporates and liquid and its vapour reach equilibrium. The difference between the heights of the mercury columns in manometer initially and at equilibrium is a measure of the vapour pressure of the liquid at that temperature.

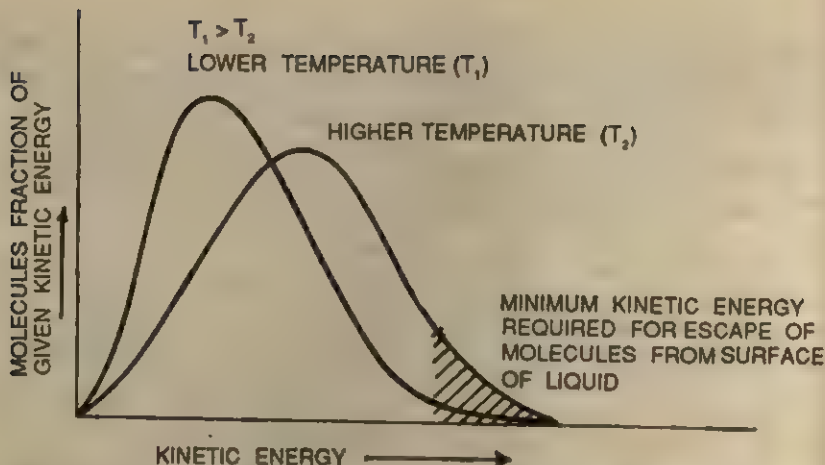
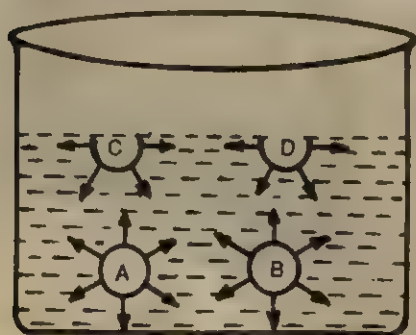


Fig. 3.41 Distribution of kinetic energies of molecules in a liquid at different temperatures.

Boiling point. This is defined as the temperature of a liquid at which its vapour pressure becomes equal to the atmospheric pressure (760 mm Hg). For example, when water is heated its vapour pressure gradually increases. At 373K, the vapour pressure of water becomes 760 mm Hg. Hence, the boiling point of water is 100°C . Similarly, boiling points of alcohol and diethyl ether are 78.5°C and 34.6°C respectively (Fig. 3.40). Liquids have their characteristic boiling points.

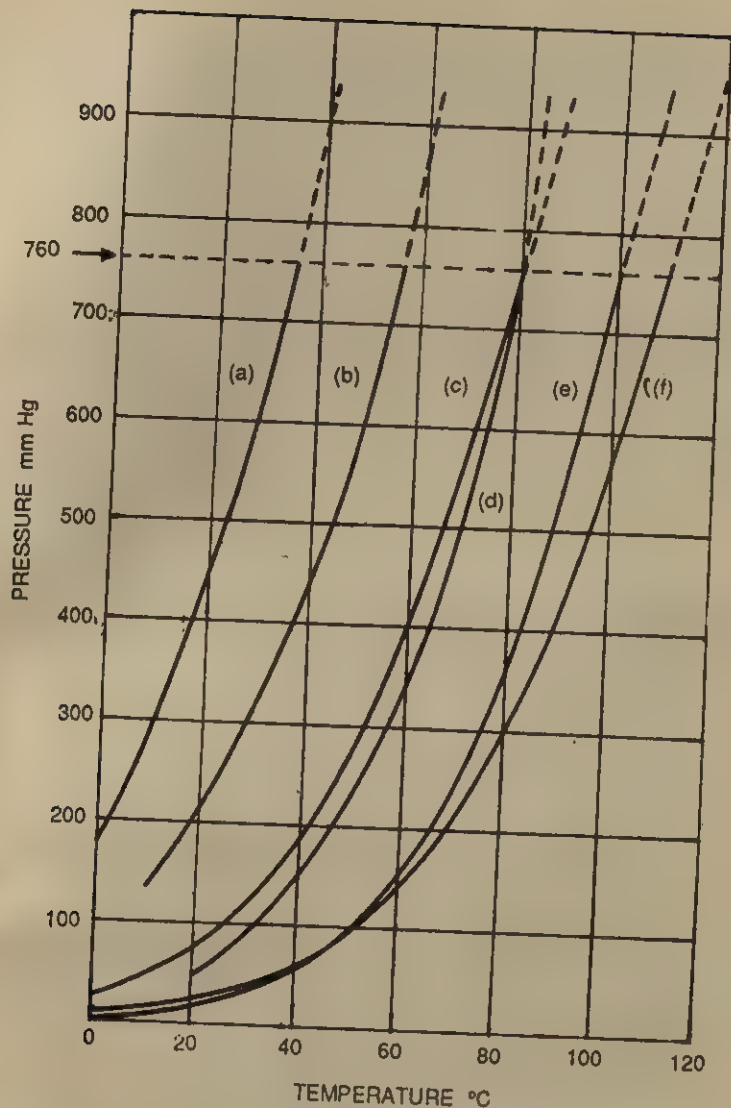
Surface tension. This property of liquids is also attributed to the intermolecular attractive forces. A molecule within the bulk of the liquid (e.g. A or B in fig. 3.42) is attracted equally from all sides by the surrounding molecules. But a molecule at the surface (e.g. C or D in fig. 3.42) is under strain or tension



because it is being pulled inward by attraction from nearby molecules. There are no liquid molecules above it to balance the forces. It is thus experiencing a resultant pull inward. All the molecules at the surface of the liquid experience this tension which is called the *surface tension* of a liquid. The surface tension of water is 72.8×10^{-3} newton/m. Different liquids have different surface tension, simply because the strength of the attractive force varies with the nature of

Fig. 3.42 Forces on molecules well within the liquid and at the surface

the liquid strength of the intermolecular attractive forces in a liquid. It is



(a)	DIFTHYL ETHER,	b.p.	34.6°	(b)	ACETONE	b.p.	56.1 °C
(c)	BENZENE	b.p.	80 °C	(d)	ETHANOL	b.p.	78.5 °C
(e)	WATER	b.p.	100 °C	(f)	TOLUENE	b.p.	111 °C

Fig. 3.40. Plots showing increase in vaour pressure of liquids with increase in temperature. Liquids boil at the temperature at which the vapour pressure is 760 mm Hg.

because of surface tension that a liquid drop assumes a spherical shape. This shape has the smallest possible surface to volume ratio. The surface tension is also responsible for the rise or fall of liquids in capillaries.

Viscosity. All liquids show some resistance (or opposition) to flow because of the intermolecular attractive forces. This is known as viscosity. Several factors affect the viscosity of a liquid, particularly the size and shape of its molecules and the strength of the attractive forces between them. A larger molecule offers more resistance to flow than a smaller one. A liquid is also likely to be viscous if the attractive forces between its molecules are strong; its molecules are less easily moved about with respect to each other. Ethanol because of hydrogen bonding is more viscous than ethyl ether. It also depends upon the molecular mass and nature of a liquid. Liquids like water, alcohol, ether, *etc.* flow readily while oils are viscous. With an increase in temperature, viscosity usually decreases because increased kinetic energy (due to increase in temperature) overpowers the attractive forces.

SELF ASSESSMENT QUESTIONS

MULTIPLE CHOICE QUESTIONS

3.1 Put a (✓) mark against the most appropriate choice

- (i) Which of the following exerts maximum pressure?
(a) 75.0 cm high column of mercury (density = 13.6 g cm^{-3})
(b) 10.0 g H_2 (g) at 20°C in a container of 20 litre volume
(c) A 60.0 cm high column of CCl_4 (density = 1.60 g cm^{-3})
(d) 32.0 g O_2 at STP contained in 10 L vessel.
- (ii) When temperature of 1 mol of a gas at 1 atm pressure is changed from 100°C to 250K the volume of the gas
(a) decreases (b) becomes double of the initial volume (c) increases, but not to twice the initial volume (d) remains constant
- (iii) A sample of N_2 (g) is collected over water at 300K at a barometric pressure of 748 mm Hg. (Aqueous tension at $300\text{K} = 25 \text{ mm Hg}$). The partial pressure of N_2 (g) in the sample collected is
(a) 25 mm Hg (b) 0.95 atm (c) 0.98 atm (d) 0.01 atm
- (iv) A 1L container has 0.1 mol H_2 (g) and 0.1 mol O_2 (g). The container has a pinhole leak. After 5 seconds in the container the partial
(a) Pressure of O_2 (g) exceeds that of H_2 (g)
(b) Pressure of H_2 (g) exceeds that of O_2 (g)
(c) Pressures of both the gases remain unchanged
(d) Pressures of both the gases increase above their initial values.
- (v) When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules:
(a) are above the inversion temperature (b) exert no attractive forces on each other

(c) do work equal to the loss in kinetic energy (d) collide without loss of energy
(IIT 1984)

(vi) If a gas is expanded at constant temperature
(a) the pressure increases (b) the kinetic energy of the molecules remains the same
(c) the kinetic energy of the molecules decreases. (d) the number of molecules of the gas increases

(vii) The volume of a gas measured at 27°C and 1 atm pressure is 10.0L. What final temperature would be required to reduce the volume to 5.0L at constant pressure.
(a) 135°C (b) 54°C (c) 150K (d) 327K

(viii) In van der Waal's equation of state for a non-ideal gas the term that accounts for intermolecular forces is
(a) $(V-b)$ (b) $\frac{a}{V^2}$ (c) RT (d) $(RT)^4$

(ix) A bottle of dry ammonia and a bottle of dry HCl (g) connected through a long tube are opened simultaneously at both ends, the NH_4Cl (s) formed will be
(a) at the centre of the tube (b) near the dry HCl (g) bottle (c) near the ammonia bottle (d) throughout the length of the tube.

(x) The temperature of a certain mass of a gas increased from 40°C to 41°C at constant pressure. The volume of the gas, will,
(a) remain constant (b) increase by $1/273$ of its volume at 273K (c) increase by $1/273$ of its volume at 40°C (d) increase but the increase in volume cannot be predicted.

(xi) The kinetic energy of one mol of any gas depends upon the
(a) nature of the gas (b) pressure of the gas (c) temperature on the kelvin scale of the gas (d) volume of the gas.

(xii) Equal masses of sulphur dioxide and oxygen are mixed in an empty container at 300K. The total pressure exerted by the gaseous mixture is 1 atm. The partial pressure exerted by sulphur dioxide gas is
(a) 0.33 atm (b) 0.5 atm (c) 0.20 atm (d) 0.67 atm

(xiii) In NaCl crystal each Cl^- ion is surrounded by
(a) 4Na^+ (b) 6Cl^- (c) 6Na^+ (d) 4Cl^-

(xiv) What structural units occupy the lattice sites in the metallic crystals?
(a) Atoms (b) Electrons (c) Negative ions (d) Positive ions

(xv) What type of crystals should be the softest and have the lowest boiling point?

- (a) Covalent crystals (b) Ionic crystals
(c) Metallic crystals (d) Molecular crystals

3.2 Fill in the blanks

- (i) Kelvin and Celsius scales are related as.....
(ii) The actual number of molecules in one gram-mol of a gas is.....
(iii) At constant pressure, volume, V , of a given mass of a gas is related to its absolute temperature, T , as $V/T = \text{constant}$. The name of this law is.....
(iv) The constant, R , is known as.....constant its value is.....joules.
(v) The average kinetic energy of 1 mol of CO_2 gas at 300K is.....
(vi) Real gases obey gas laws approximately at.....pressures and.....temperatures.
(vii) Space lattices of different kinds of constituent particles in a crystal may not always, be....., however in NaCl, the two.....are identical.
(viii) Most crystals show good cleavage because the atoms, ions or molecules in a crystal are.....
(ix) In a molecular crystal the forces holding together the atoms within a molecule are.....
(x) Experimental evidence for the orderly arrangement of atoms in crystals is given by.....

3.3 Point out the correct statements of the following

- (i) Kinetic energy of a molecule is zero at 0°C . (IIT 1985)
(ii) A gas in a closed container will exert much higher pressure due to gravity at the bottom than at the top. (IIT 1985)
(iii) The rate of diffusion of a gas is inversely proportional to the square root of its density.
(iv) The ratio of PV to T is independent of the pressure for a given quantity of an ideal gas.
(v) An ideal gas would have zero volume at 0 K.
(vi) At low pressures the molecules of a gas are moving at a lower speed than that of at high pressures.
(vii) All molecules of a gas move with the same speed.
(viii) Amorphous solids are super cooled liquids.
(ix) In crystals short range order exists.
(x) Unit cell is the simplest building unit in crystals.

3.4 Match the following choosing one item from column X and the appropriate item from column Y

Column X	Column Y
(i) $\frac{n}{N}$	(a) Average kinetic energy of 1 mol of a gas
(ii) Molecules are not points but have definite volume	(b) Metallic crystals
(iii) $P = P_1 + P_2 + P_3$	(c) Kinetic gas equation
(iv) $3/2 RT$	(d) 0°C
(v) 1.987 calories	(e) Mole fraction
(vi) $PV = 1/3 mn\bar{C}^2$	(f) Dalton's law of partial pressure
(vii) 273.15K	(g) X-ray study
(viii) Positive ions in a sea of electrons	(h) Real gases
(ix) Substances with similar crystal forms	(i) Isomorphous
(x) Crystal lattice	(j) R

SHORT ANSWER QUESTIONS

- 3.5 Two gas jars A and B are of equal volumes and contain an equal mass of H_2 (g) and O_2 (g) respectively. Gas jar A is maintained at 300K and B at 600K. Compare the two samples quantitatively with respect to
 - (i) number of molecules
 - (ii) average speed of molecules
 - (iii) average kinetic energy of molecules
- 3.6 Using the ideal gas equation derive an equation relating molecular weight to density, pressure and temperature of the gas.
- 3.7 Why is the density of ice lower than that of water?
- 3.8 Which of the followings would diffuse most quickly under comparable conditions?
 H_2O , HDO or D_2O
- 3.9 Why does the pressure build up in a tyre on a hot day?
- 3.10 A particular gas sample is 1% oxygen molecules. How many oxygen molecules are there in one litre of the gas sample at STP?
- 3.11 The molar volume of a gas is affected by pressure and is quite low at high pressure. The density of CO_2 (g) at 483K and 30 atm is 0.084 g/cm^3 .
 - (i) Calculate the molar volume of CO_2 (g) at these conditions.
 - (ii) How many molecules does this volume contain.
- 3.12 A nitrogen gas volume thermometer has a volume of 100 cm^3 when immersed in an ice-water at 0°C . When immersed in liquid bromine, the volume of the nitrogen at the same pressure is 120 cm^3 . Calculate the temperature of liquid bromine in $^\circ\text{C}$ and K.
- 3.13 A certain solid has m.p. 1100°C . It is a nonconductor. Which type of solid is it likely to be? How could you make a final decision about the type of solid?
- 3.14 Classify each of the followings as molecular, ionic or metallic solids
 - (i) Ba
 - (ii) BaO
 - (iii) CO
 - (iv) SiH_4
 - (v) $NaNO_3$
- 3.15 What is the wavelength of an X-ray beam which gives a first order reflection at an angle of 23° from a crystal with spacing at 2.20 \AA ?

TERMINAL QUESTIONS

- 3.1 How do you combine Boyle's law, Charles' law, and Avogadro's hypothesis into one equation?
- 3.2 What happens to the total pressure when gases are mixed in a given volume?
- 3.3 How does average gaseous molecular speed vary with temperature?
- 3.4 Explain on the basis of the kinetic molecular theory, why most gases cool on expansion into a vacuum.
- 3.5 A balloon has a volume of 2.0 litres indoors at a temperature of 298K. If it is taken out at night when the temperature is 244K, what will its volume be? (Ans 1.64L)
- 3.6 How many millilitres of CO_2 at 303K and 700 torr must be added to a 500 ml container of N_2 at 293K and 800 torr to give a mixture having a pressure of 900 torr at 293K? (73.9 mL)
- 3.7 At what temperature will the average molecular speed in a gas be double its value at 0°C . Does this vary with the nature of the gas? (819°C) ? ? ?
- 3.8 Explain the following:
 - (i) Alkali metals are soft and malleable whereas most of the transition metals are hard and some are brittle.
 - (ii) Metals conduct electricity whereas the non-metals do not.
 - (iii) While melting a solid substance, the temperature does not rise until all the solid has melted.
 - (iv) Melting point of a solid depends upon the mutual attractive forces between its building units.
 - (v) Fluorine and chlorine are gases at ordinary temperature, bromine a liquid and iodine a solid.

- 3.9 (a) Arrange the following compounds in the expected order of increasing melting point : NaF, NaCl, NaBr and NaI. Give the reason for your arrangement.
 (b) Arrangements for the closest packing of spheres are possible in two ways. Explain.
- 3.10 (a) How many nearest neighbours are there in the hcp, fcc and bcc around the central atom ?
 (b) Suggest schemes through the packing of spheres which lead to bcc and hcp packing.
- 3.11 List the various lattices. Give an example of each and account for the differences in hardness and melting point of each.
- 3.12 Describe cubic close packing. Mention the other two usual cubic close packings with two compounds of each representing the packings. What will be the coordination number of each sphere in cubic close packing ?
- 3.13 How many types of unit cells are adopted by crystals ? Draw the sketch for any four of them. Also suggest the name of crystals having these four unit cells.
- 3.14 Caesium chloride has a density of 3.940 g cm^{-3} . Calculate the size of unit cell and the interionic distance (At. wt of Cs = 132.9, Cl = 35.5)
 (Ans. The length of the side of the unit cell cube is 4.14 \AA ; interionic distance = 3.58 \AA)
- 3.15 If the interionic distance in NaCl is 3.57 \AA predict the angle at which a first order reflection of X-rays of wavelength 1.75 \AA will occur (Ans $\theta = 14^\circ$).
- 3.16 Write short notes on the following characteristics of liquids :
 (a) Surface tension, (b) viscosity, (c) vapour pressure, and (d) diffusion.

ANSWERS TO SELF ASSESSMENT QUESTIONS

- 3.1 (i) b (ii) a (iii) b (iv) a (v) b (vi) b (vii) c (viii) b (ix) b (x) c (xi) c (xii) a (xiii) c (xiv) d (xv) d
- 3.2 (i) $K = 273.15 + t^\circ\text{C}$
 (ii) 6.02×10^{23}
 (iii) Charles law (iv) gas, 8.314 J
 (v) 3.741 kJ (vi) low, high (vii) identical, space lattices
 (viii) arranged in planes (ix) covalent bonds
 (x) X-ray diffraction patterns
- 3.3 (i) F (ii) F (iii) T (iv) T (v) T (vi) F
 (vii) F (viii) T (ix) F (x) T
- 3.4 (i) e (ii) h (iii) f (iv) a (v) j (vi) c
 (vii) d (viii) b (ix) i (x) g
- 3.5 (i) Let the mass of H_2 and O_2 be w g each

$$n_{\text{H}_2} = w/2 \text{ and } n_{\text{O}_2} = w/32$$

As the number of moles of H_2 is 16 times more than that of number of moles of O_2 . Jar A containing $\text{H}_2(\text{g})$ has 16 times more molecules than that present in jar B.

- (ii) $1/3 m n C^2 = RT$ or $C^2 \propto T/M$ (R is a constant)

$$\frac{\text{Average speed of } \text{H}_2 \text{ molecules}}{\text{Average speed of } \text{O}_2 \text{ molecules}} = \sqrt{\frac{300}{2} \times \frac{32}{600}} = \sqrt{2}$$

- (iii) $\text{K.E} \propto T$

$$\frac{\text{K.E. of } \text{H}_2 \text{ molecules}}{\text{K.E. of } \text{O}_2 \text{ molecules}} = \frac{300}{600} = 0.5$$

3.6 $PV = nRT$

$$PV = \frac{WRT}{M}$$

$$P \frac{W}{V} = \frac{RT}{M}; \quad \frac{W}{V} = \text{density (} \rho \text{)}$$

$$P = \rho \frac{RT}{M} \quad \alpha \quad M = \rho \frac{RT}{P}$$

- 3.7 In ice, each oxygen atom is surrounded tetrahedrally through H-bonds to four water molecules. The resulting structure is a very open one and this explains why the density of ice is lower than that of water.
- 3.8 The lightest of all, H_2O would diffuse most quickly.
- 3.9 As the temperature of air inside the tyre increases, the kinetic energy increases. Since the volume of the tyre remains almost constant, the increased kinetic energy results in more collisions per unit time with the tyre walls, and the force exerted per collision is greater. Thus the pressure rises.
- 3.10 22.4 L of the gas sample at STP has 6.02×10^{23} molecules. Therefore, 1L gas sample having 1% oxygen molecules in it would have O_2 molecules
 $= 6.02 \times 10^{23}$
 22.4×100
 $= 2.68 \times 10^{20} O_2 \text{ molecules/L}$
- 3.11 (i) Molecular mass of CO_2 is 44
 Therefore molar volume $= \frac{44}{0.084}$
 $= 523.8 \text{ cm}^3 \text{ mol}^{-1}$
 $= 0.52 \text{ L mol}^{-1}$
- (ii) 6.02×10^{23}
- 3.12 $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ at constant pressure
 $\frac{V_1}{T_1} = \frac{100 \text{ cm}^3}{0^\circ\text{C} = 273\text{K}}$ $\frac{V_2}{T_2} = \frac{120 \text{ cm}^3}{T_2 = ?}$
 Substituting the values
 $T_2 = \frac{V_2}{V_1} \cdot T_1 = \frac{120}{100} \times 273 = 327.6\text{K}$
 $= 54.6^\circ\text{C}$
- 3.13 It could be ionic or macromolecular. Test conductivity of melt. Ionic solid melt would be good conductor.
- 3.14 (i) metallic (ii) ionic (iii) molecular (iv) molecular (v) ionic
- 3.15 You know $n\lambda = 2d \sin\theta$
 hence $n = 1$, $d = 2.20 \text{ \AA}$
 $\lambda = ?$ $\theta = 32^\circ$
 $\lambda = \frac{2 \times 2.20 \sin 23}{1} = \frac{2 \times 2.20 \times 0.391}{1} = 1.72 \text{ \AA}$

UNIT 4

ATOMIC STRUCTURE

.....The philosopher should be a man willing to listen to every suggestion, but determined to judge for himself. He should not be biased by appearances, have no favourite hypothesis, be of no school, and in doctrine have no master. He should not be a respecter of persons but of things. Truth should be his primary object. If to these qualities be added industry, he may indeed hope to walk within the veil of the temple of NATURE.

MICHAEL FARADAY
(1791-1867)

UNIT PREVIEW

- 4.1 Introduction
- 4.2 Constituents of the atom
 - 4.2.1 Discovery of cathode rays (electrons)
 - 4.2.2 Millikan's determination of the charge of an electron.
 - 4.2.3 Discovery of positive rays (protons)
 - 4.2.4 Radioactivity
 - 4.2.5 Thomson's model of atom
 - 4.2.6 Rutherford's experiment and the nuclear atom
 - 4.2.7 Discovery of neutron
- 4.3 Atomic number
 - 4.3.1 Mass number
 - 4.3.2 Isotopes
- 4.4 Electronic structure of atoms
 - 4.4.1 The nature of light
 - 4.4.2 Light and energy
 - 4.4.3 Interference and diffraction
 - 4.4.4 Photoelectric effect and the particle nature of light
 - 4.4.5 Atomic spectra
 - 4.4.6 Atomic spectra and Rutherford's model
 - 4.4.7 Bohr's model of the hydrogen atom — A particle model
Significance of Bohr's postulates; shortcomings of Bohr's model
 - 4.4.8 Quantum mechanical model of the atom — de Broglie concept; uncertainty principle
 - 4.4.9 Quantum numbers
 - 4.4.10 Pauli's exclusion principle
Evidence for sub shells
 - 4.4.11 Shapes for orbitals
 - 4.4.12 Electron configuration of atoms (Aufbau principle)
Stability of filled and half-filled orbitals

Self assessment questions

Terminal questions

Answers to self assessment questions

LEARNING OBJECTIVES

At the completion of this unit, you should be able to,

1. Give the postulates of the Dalton's atomic theory
2. Cite the experimental evidence for the existence of electrons, protons and neutrons as fundamental particles of atoms.
3. Account for the mass of an atom through the existence of neutrons
4. Understand the phenomenon of radioactivity.
5. Explain the observations made with Rutherford's experiment and his nuclear atomic model, i.e., the presence of a small nucleus containing most of the mass and all of the positive charge in the atom, around which electrons move.
6. Determine the number of each of the fundamental particles in an atom from the atomic number and mass number.
7. Describe the nature of light and electromagnetic waves.
8. Describe the photoelectric effect and state which mode of light it supports.
9. Correlate quantized energy states - ground states and excited states - in atoms with the origin of line spectra.
10. Describe the Bohr's model of the atom.
11. Explain quantized energy states in terms of Bohr's orbits and electron transition between orbits.
12. Calculate the wavelength, frequency, and energy changes associated with the electron transitions, including ionization in the hydrogen atom on the basis of the Bohr's model.
13. Describe the wave properties of matter and make calculations of the wave-length of particle from their mass and velocity.
14. State the restrictions placed on our ability to know the position and momentum of a small particle.
15. Comment on the contributions of de Broglie.
16. Explain the results of calculation, from the wave mechanical model of the hydrogen atom in terms of orbitals and probable electron density.
17. List the four quantum numbers that define the energy state of the electron in a hydrogen atom along with their possible values and state their physical significance in terms of orbitals.
18. Calculate the maximum number of electrons that can occupy each quantum energy level in an atom.
19. List the symbols that represent energy sublevel in atoms.
20. Explain the significance of the Pauli's exclusion principle in relation to the electron structure of atoms.
21. Draw the shapes of s, p and d orbitals.
22. Sketch the probability regions about an atomic nucleus that illustrate the different energy levels.
23. State the relative energies of the orbitals in multielectron atoms.
24. Write the electron configuration of an atom with the help of its atomic number and determine the number of any unpaired electrons present.
25. Illustrate the electronic configuration of atoms by pictorial representation.

4.1 INTRODUCTION

From the early times of civilization, philosophers have debated the divisibility of matter. Could a small piece of matter be divided again and again into infinitely small particles - the concept Aristotle documented - or was there a limit to this divisibility as Lucveitus and Democritus had proposed ? These Greek philosophers have been very active in debating and proving their view point. But they were forced to

restrict testing their ideas almost exclusively to mental exercise and logic rather than experiment.

Around 400 B.C., Democritus suggested that all matter is composed of small, discrete, indivisible particles called atoms (from the Greek word 'atomos' meaning indivisible). His ideas were rejected for 2000 years, but they began to make sense in the late eighteenth century. After all, it was their word which John Dalton in the early 1800 years used as he developed his atomic theory to explain natural phenomena and chemical reactions. But were the Greek atomists right? It all depends upon the meaning of the word, "indivisible". It is true that atoms are of fundamental importance. But it is certainly not true that atoms are indivisible. It is evident from the recorded history that Dalton changed his mind before the end of his life and in a remarkable prophesy suggested that a great deal of energy might be liberated if atoms could be split.

John Dalton summarized and supplemented the concepts of Greek philosophers and scientists which are the core of 'Dalton's Atomic Theory'. In the condensed form Dalton's postulates are as given below:

1. Matter (or element) is composed of tiny fundamental particles called atoms.
2. Atoms of an element are similar (same mass and size) but differ from atoms of other elements.
3. Atoms enter into combinations with other atoms of different elements or same element to form compounds in simple numerical ratios.
4. Atoms are indestructible and cannot be created or transformed into atoms of another element.
5. In a given compound the relative number and kind of atoms are constant.

Throughout the nineteenth century chemists and physicists kept on harping on the Dalton's belief that atoms were small and hard indivisible spheres and gave no consideration to the possibility that they might have an internal structure. Towards the end of the nineteenth century, experimental evidence established that an atom can be subdivided.

It is now known that all atoms are composed of three fundamental particles, the proton, the neutron and the electron. According to modern theory, an atom (radius about 10^{-10} m) consists of two parts, i.e. the nucleus (radius about 10^{-15} m) and the extra-nuclear part. The nucleus is composed of protons and neutrons; in a neutral atom the number of protons is equal to the number of electrons in motion about the nucleus. Both the proton and the neutron have almost the same mass as the hydrogen atom (~ 1 amu), whereas the electron has about $1/1848$ (0.000546 amu) of this mass. The charges on the proton and electron

are equal in magnitude though opposite in sign, that on the electron being negative. The neutron has no charge.

The number of neutrons in the nuclei of the atoms is usually not the same as the number of protons. The difference in the masses of atoms of elements are the result of the differences in the composition of the nuclei of the atoms. This variation in composition of the nuclei of the atoms accounts for the existence of isotopes (same number of protons but different number of neutrons) of an element. The number of protons in the nucleus of an atom is called the atomic number.

The discovery of fundamental particles led to a modification of the Daltonian picture of an atom. It has helped to systematize chemical facts in ways that enhance our understanding of internal structure of atom. The discovery of electron had a strong bearing on the laws of classical physics (Newtonian mechanics) which were at one time, thought of as universal truth. They failed to describe the motion of electrons correctly. This resulted in the formulation of a mechanics called 'quantum mechanics'.

The observations that led to a gradual refinement and extension of the atomic theory are numerous indeed, a detailed description of all of them is beyond the purpose of this book. However, a brief account of some of the more significant breakthroughs is given here.

4.2 CONSTITUENTS OF THE ATOM

During the early 1800s, a number of scientists, most notably Humphry Davy and his assistant and successor, Michael Faraday (1791-1867) established the electrical nature of matter. The earliest evidence for the electrical nature of matter was provided by combing of hair.

A comb acquires the ability to attract small pieces of paper and similar objects to its surface, after it has passed through dry hair. It was also established that substances like glass rod or ebonite rod when rubbed with silk or animal fur generated electricity. These experiments reveal that two types of charges exist. Benjamin Franklin is responsible for introducing the arbitrary convention that the electrical charge is 'negative' when it has been generated from ebonite rubbed with animal fur, whereas the charge is 'positive' when it has been generated from glass rubbed against silk.

In the 1830s Faraday studied the decomposition of salts, acids and bases by passing an electrical current through them. He summarized his observations in the form of two laws of electrolysis :

1. The amount of a substance produced in a chemical change is directly proportional to the amount of electricity passed during electrolysis, i.e.,

$$m \propto Q$$

$$\text{or } m \propto It \quad (Q = It)$$

$$\text{or } m = Z It$$

where m = mass of the ions liberated or consumed, Q = quantity of electricity in coulombs, I = current passed in amperes, t = time in seconds and Z = constant of proportionality. Z is taken as equal to electrochemical equivalent and is equal to the amount of the product when 1 ampere current is passed for one second, i.e., one coulombs of charge.

2. When the same quantity of electricity is passed through different electrolytes, the amounts of the various substances liberated or produced at the electrodes are in the ratio of their equivalent masses.

We know that one g equivalent of any substance requires one mole of electrons to react. Further, one faraday is the amount of charge equal to one mole of electrons.

Thus, one Faraday, $F = N e = 6.023 \times 10^{23} \times 1.602 \times 10^{-19} = 96500 \text{ coulombs mol}^{-1}$.

It is observed that when one faraday of electricity is passed through molten sodium chloride, 1 g equivalent or 23g of sodium atoms or 1 mole of sodium is deposited at the cathode and 1/2 mole of chlorine (Cl_2) gas is evolved at the anode. These amounts remain fixed as long as the amount of electricity is one faraday. This is in agreement with the first law. The mole ratio is 2:1 which is in agreement with the second law.

Neither Davy nor Faraday had to do anything with the structure of atom. Faraday's results, however, suggested to George Stoney that an electric current, like matter, is composed of small units. In 1891, Stoney proposed the name, electron, from elektron, the Greek word for amber, a fossil resin that becomes electrically charged when rubbed with wool or silk.

4.2.1 Discovery of Cathode Rays (Electrons)

One of the first significant advances, after the Dalton's atom, was made by J.J. Thomson (1898) and Lenard. They passed electric discharges through gases. This led to the discovery of negatively charged particles. Basically, their device consists of a closed glass tube, into the ends of which are sealed two metal plates to serve as electrodes. A high voltage (5000 — 10,000 volts) is imposed across the electrodes (Fig. 4.1). If the air (or other gas say neon, mercury vapour, helium, etc.) in the tube is at atmospheric pressure, nothing is observed.

However, if most of the air is pumped out of the tube, the remaining air begins to glow and conducts the electric current. On lowering the pressure, the appearance of the tube changes. At sufficiently low

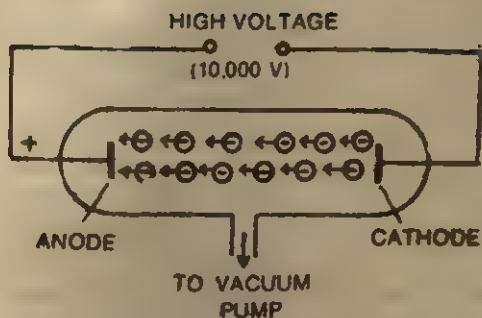


Fig. 4.1 Formation of cathode rays. Electrons are flowing from cathode to anode in a gas discharge tube.

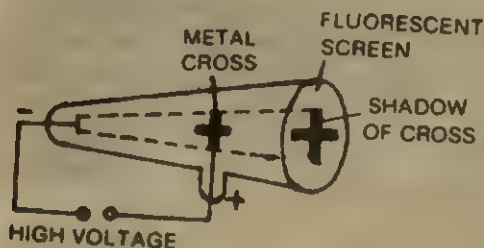


Fig. 4.2. Cathode rays travel in straight lines and cast shadow of the object placed in their path upon the wall opposite the cathode.

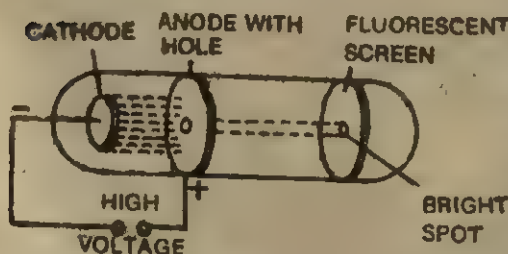


Fig. 4.3 : Movement of cathode rays. They move in straight lines and originate at the cathode.

pressure, the glow fades, although current continues to flow and the end of the glass tube with anode (the positive electrode) fluoresces (emits lights). The fluorescence at the anode of the tube is caused by the rays emerging from the cathode and moving towards the anode. These rays are called cathode rays because they originate at the cathode.

Thomson performed a series of experiments that permitted him to illustrate the important features of cathode rays. Their results are noted below:

1. The cathode rays travel in straight lines. When a metallic object is placed in the path of the cathode rays, a shadow is cast upon the wall opposite the cathode (Fig. 4.2).

Also, if a metal plate (Fig. 4.3) with a hole (anode) in it is placed in front of the cathode, and the other end opposite the cathode is coated with a fluorescent substance, a bright spot of light can be seen.

The shadow of the metal object on the wall opposite the cathode and the size of the spot on the

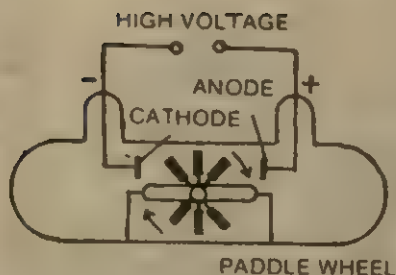


Fig. 4.4. Cathode rays impart mechanical motion to a paddle wheel placed in their path. They possess kinetic energy.

fluorescent screen compared to the size of the hole (in the anode) show that cathode rays travel in straight lines.

2. The cathode rays consist of particles. If a paddle wheel is placed in the path of the rays, it starts rotating (Fig.4.4). This movement establishes that cathode rays consist of particles which can impart their momentum to the wheel.

3. The cathode rays consist of negatively charged particles. A magnet placed outside the tube causes the spot of light to move at right angles to the direction of the magnetic field (Fig. 4.5). The direction of the deflection suggests that the cathode rays carry a negative electric charge. The cathode rays, when pass through a strong electric field, experience deflection (Fig.4.6). They move towards the positively charged electrode. This also shows that the rays carry a negative charge.

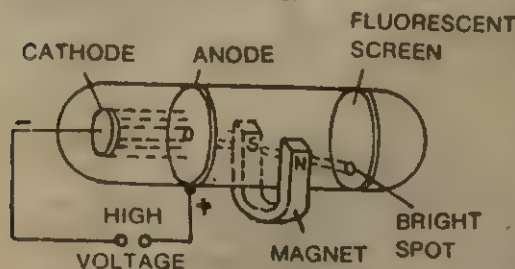


Fig. 4.5 Effect of a magnetic field on cathode rays. They are deflected by a magnetic field. The downward deflection shows that the cathode rays are negatively charged.

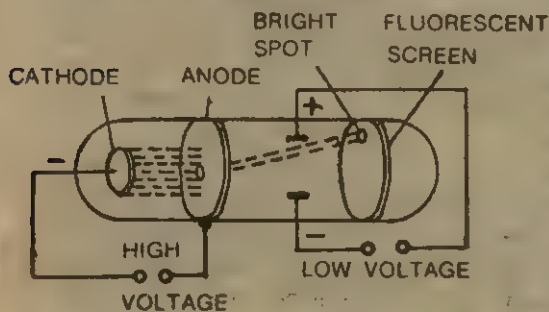


Fig. 4.6 Effect of an electric field on cathode rays. They are deflected by an electric field.

electrodes and gases used. J.J. Thomson studied the behaviour of these rays by passing them through both magnetic and electric fields. He adjusted the field such that the cathode rays strike the fluorescent screen at the same spot when neither field is present (Fig. 4.7). Thom-

4. The cathode rays have same e/m irrespective of the nature of

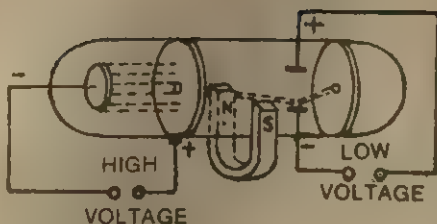


Fig. 4.7 An assembly for the measurement of e/m for the particles constituting cathode rays.

son measured the ratio of the electric charge ' e ' to mass ' m ' of the particles in cathode rays by using this experiment.

Thomson performed a series of experiments by using different metals for electrodes and different gases in the tube. In all the arrangements, the charge to mass ratio, e/m for cathode rays was found to be the same.

This establishes that such negative particles form a common constituent of all gases. This has been found to hold good for other form of matter also. The value of e/m was found to be 1.76×10^8 coulomb/g and the particles were identified as electrons.

4.2.2 Millikan's Determination of the Charge of an Electron

Measurement of the charge, e on the electron which permitted calculation of its mass from the value of e/m was made by Robert Millikan an American Physicist. In an ingenious experiment (Fig. 4.8) Mil-

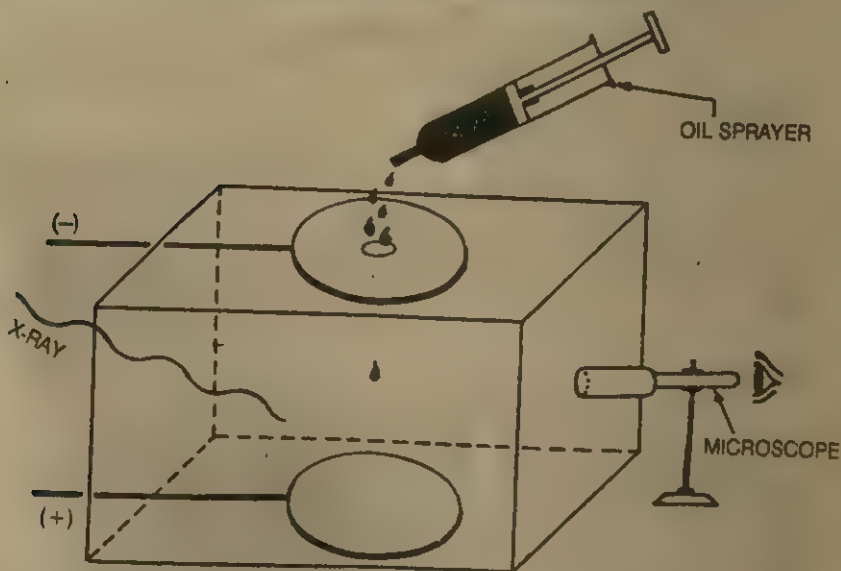


Fig. 4.8 Millikan's experiment for determination of charge of electron.

likan sprayed a fine mist of oil drops above a pair of metal plates. As the droplets found their way through a hole in the upper metal plate, the air between the plates was irradiated with X-rays. X-rays knocked electrons from nitrogen and oxygen (from air). Some of these electrons collided with the oil droplets and finally molecules got attached to them; thereby imparting negative charges to the oil droplets.

He applied electric field on the plates (upper plate positive and lower plate negative) and then measured its effect on the rates at which charged oil droplets fall under the influence of gravity. He found that the downward motion of negatively charged drops could be slowed or stopped. He observed an individual oil droplet with a microscope and adjusted the charge on the plates until the force acting on the oil droplet due to the charged plates just balanced the force due to gravity.

With the knowledge of the mass of a drop - measured by observing its rate of fall in the absence of electric field and the quantity of charge on the plates required to keep the drop suspended, Millikan calculated the quantity of charge on the drop. He performed this experiment many times. He observed that the quantity of charge on the oil drop was $1.6 \times 10^{-19}\text{C}$ or an integral multiple of this charge since the oil drops could only pick up whole numbers of electrons. This suggested that the charge on the electron is $1.60 \times 10^{-19}\text{C}$. Using this value and Thomson's value for the ratio of charge to mass, we can calculate the mass of the electron.

$$e/m = 1.76 \times 10^8 \text{ C/g}$$

Solving for m , the mass of the electron, we get,

$$m = \frac{e}{1.76 \times 10^8 \text{ Cg}^{-1}}$$

Substituting $e = 1.6 \times 10^{-19}\text{C}$ gives

$$\begin{aligned} m &= \frac{1.6 \times 10^{-19}\text{C}}{1.76 \times 10^8 \text{ Cg}^{-1}} \\ &= 9.11 \times 10^{-28}\text{g} \text{ or } 9.11 \times 10^{-31}\text{kg} \end{aligned}$$

This experiment suggests that all particles contain the same charge. It also provides the conclusive proof for the existence of electrons.

4.2.3 Discovery of Positive Rays (Protons)

If electrons are observed near the anode in a discharge tube, isn't it logical to expect positively charged particles near the cathode? Actually, a radiation of this type has been observed by Eugen Goldstein (1886). He employed a discharge tube with perforated cathode as illustrated in Fig. 4.9 and observed glow (at low pressure) at the end of the tube beyond the cathode. This glow was caused by the rays emanating through the perforated cathode. These rays were called canal rays by

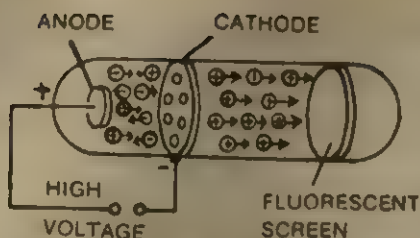


Fig. 4.9 Formation of canal rays.

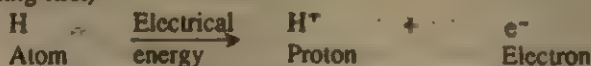
Goldstein, since they moved towards cathode and finally passed through the holes (or canals) in the cathode. Unlike the cathode rays (which are not apparent unless they strike an object that fluoresces, such as glass), canal rays possess a luminosity of their own. Furthermore, the

colour of the luminosity changes with the gas contained in the tube. Wilhelm Wien investigated Goldstein's observations thoroughly and showed that canal rays are consisted of particles which are deflected towards the negative pole in an electric field and must, therefore, be positively charged. Wien determined the charge to mass ratio of these particles using a technique similar to the one which Thomson employed in the studies of electrons. He obtained different results depending on the nature of the gas contained in the discharge tube. The charge to mass ratio for these particles was found to be much smaller than e/m for electrons. The value is maximum for hydrogen atom. The characteristics of cathode and canal rays are given in Table 4.1

TABLE 4.1 Properties of cathode and canal rays

Cathode rays	Canal rays
Composed of negatively charged particles, called electrons	Composed of positively charged ions
Move in straight lines	Move in straight lines
Possess kinetic energy and momentum	Possess kinetic energy and momentum
e/m of their particles is always the same	e/m of their particles depends upon the nature of gas

When an electron is removed from hydrogen atom, the positive particle left behind is called a proton (from the Greek word 'protos' meaning first)



The proton is a fundamental particle and a constituent of all atoms whose charge is equal to that of the electron, but opposite in sign. The mass of a proton is equal to the mass of a hydrogen ion, i.e., 1.67×10^{-27} kg (1.007 amu).

4.2.4 Radioactivity

In 1896, Henri Becquerel made a discovery that ultimately gave a

clear understanding about the arrangement of the constituents within the atom. Becquerel accidentally found that radiation was given off by uranium salts exposed to bright sunlight. He happened to see the marks of uranium sample when he developed a photographic plate that has been wrapped in a black paper to protect from the light and kept in the same place as the uranium salt. Since no light could penetrate the wrapping, he concluded that the plate has been fogged by some rays coming from a uranium salt. This phenomenon was called **radioactivity** and the substance emitting the radiation was called **radioactive**.

Nature of Radiations

The radioactive emanations from radioactive elements and their salts have been found to consist of three types of radiations (or rays), alpha (α), beta (β), gamma (γ). Rutherford, during a long series of experiments, elucidated their nature. It was found that a part of the radiations was absorbed readily, whereas the rest of the radiations emitted without any difficulty. On passing the radiations through magnetic (Fig. 4.10) and electric fields (Fig. 4.11) radiations were found to be composed of three fundamentally different kinds of emanations α , β and γ . The characteristic properties of these radiations are given below:

(a) α -Rays : These consist of material particles possessing a mass four times and a positive charge twice that of the proton. Thus, these particles are helium nuclei. These particles have the ability to ionize gases and penetrate matter. A thin layer of solid matter such as paper (Fig. 4.12) or glass can stop them. Therefore, these particles hardly penetrate into living system. The initial velocity of α -particles on emission is very high and range $1.2 \times 10^7 \text{ ms}^{-1}$ to $3.2 \times 10^7 \text{ ms}^{-1}$.

They experience small deflections in a magnetic field due to their heavy mass and large momentum. They are highly energetic particles.

(b) β -Rays: These consist of particles with a negligible mass and a unit negative charge. These are identical with electrons moving with a velocity of $9.6 \times 10^7 \text{ ms}^{-1}$ to $25 \times 10^7 \text{ ms}^{-1}$. Their energy is lower than α -particles. These rays can also ionize gases, affect a photographic plate and penetrate matter. Their penetrating power is about 100 times more than α -particles and their ionizing power is 1/100 as that of α -particles because of their extremely low mass. They can be stopped by thin sheets of metal. These particles can penetrate into the tissues to the extent of 1 cm or slightly more. They deflect through a large angle in a magnetic field due to their small mass and comparatively very small momentum.

(c) γ -Rays: These are photons of very high energy. They travel with the velocity of light. They are totally unaffected by electric and

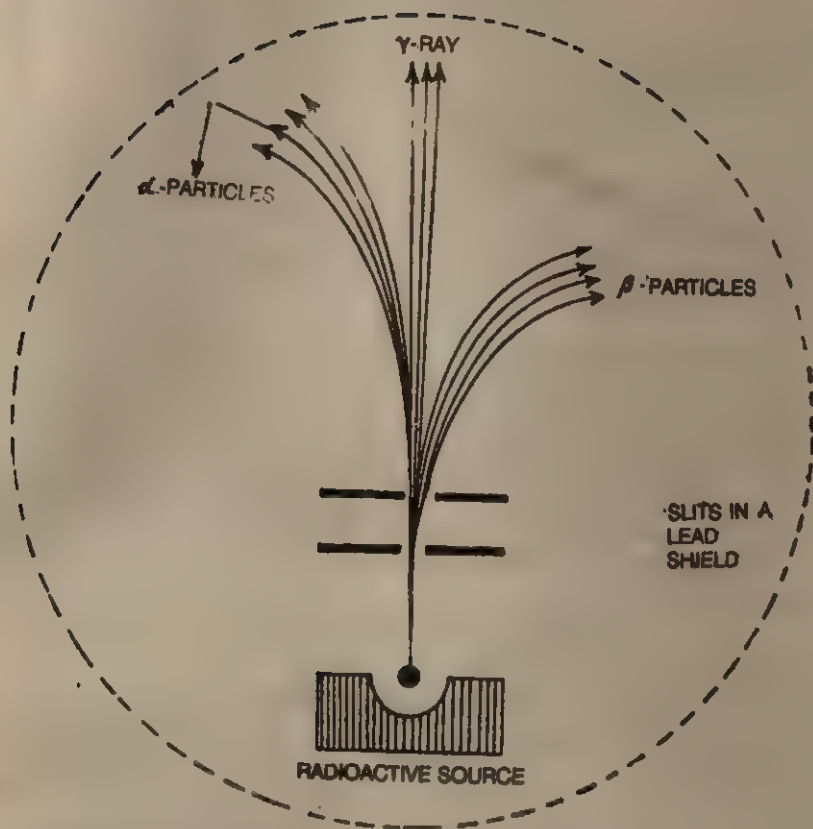


Fig. 4.10 Effect of a magnetic field on radiations

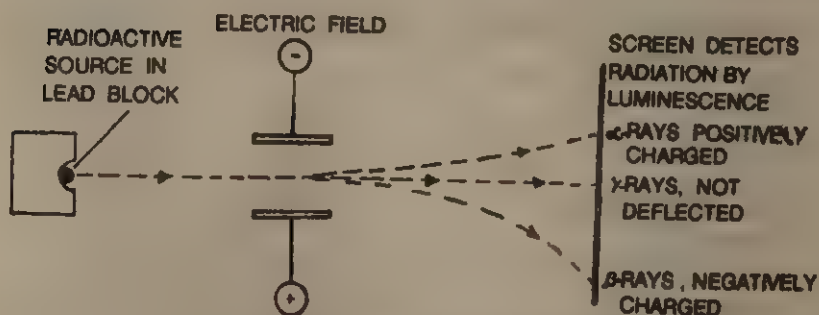


Fig. 4.11 Effect of an electric field on radiations

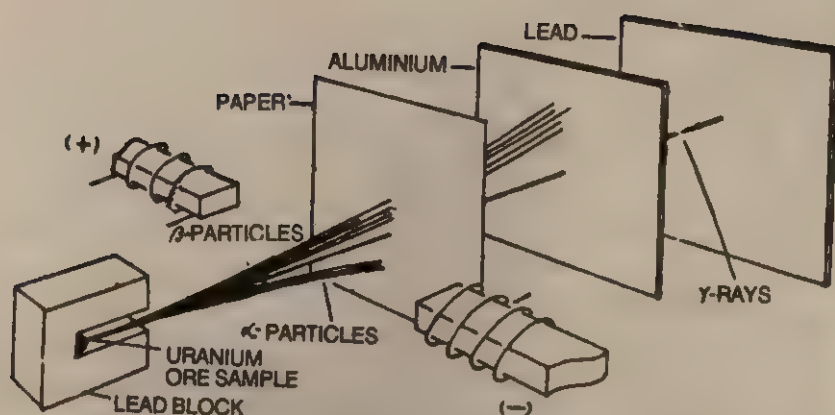


Fig. 4.12 Relative penetrating powers of alpha, beta and gamma radiations

magnetic fields. These rays are electromagnetic radiations of very short wavelength. These are similar to X-rays, but of even higher energy. They also affect photographic plates, ionize gases and penetrate matter. They penetrate about 10 to 100 times more than β -rays. Their ionizing power is very low (1/100th of that of β -particles).

Properties of these three types of radiations are summarized in Table 4.2

TABLE 4.2 : The radioactive radiations

Properties	α -Rays (α -particles)	β -Rays (β -particles)	γ -Rays
Charge	Positive (+2)	Negative (-1)	Natural
Mass number	4	0	0
Approximate mass H = 1	4	$\frac{1}{1840}$	0
Nature	Helium nuclei, ${}^4_2\text{He}$ (2 protons 2 neutrons)	Electrons (1 electron), $-1e$	Electromagnetic radiations
Velocity	$1-2 \times 10^7$ to $3.2 \times 10^7 \text{ ms}^{-1}$	9.6×10^7 to $25 \times 10^7 \text{ ms}^{-1}$	$3 \times 10^8 \text{ ms}^{-1}$ (velocity of light)
Relative effect of electric and magnetic fields	Small deflection	Large deflection	No deflection
Energy	High	Low	Very high
Relative penetrating power	1	100	1000
Range in air	Short range a few cm	Intermediate a few m	Long range a few km
Approximate thickness of Al sheet penetrated by radiations	0.002 cm	0.2 cm	100 cm
Approximate tissue penetration	0.01 cm	1 cm	100 cm
Approximate comparative ionizing power	10000	100	1

4.2.5. Thomson's Model of Atom

The discovery of electron and proton provided evidence against the indivisibility of atom. It was now natural for the scientists to think of the structure of atom. A hydrogen atom could now be considered to consist of two parts—a positively charged proton, accounting for all the mass of atom, and a negatively charged electron.

Around the turn of the century, several attempts were made to extend this model of the hydrogen atom to a general one that would apply to all atoms. One such model was created by Thomson in 1904. He regarded the atom as consisting of a diffuse cloud of positively charged body (positive charge is uniformly spread throughout the spherical volume of the atom) in which negatively charged electrons are embedded throughout (Fig. 4.13). This has been referred to as the 'plum pudding model' by Thomson. His model could explain the phenomena of cathode ray production, light emission and ionization. However, no quantitative explanation could be achieved of these phenomena.

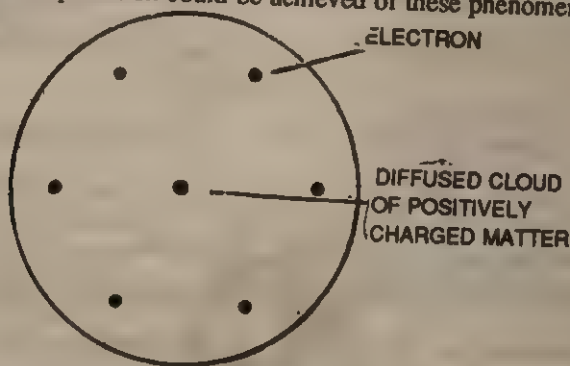


Fig 4.13 Thomson's model of atom

4.2.6 Rutherford's Experiment and the Nuclear Atom : (The Scattering of α -Particles)

Sir Ernest Rutherford (1911) directed a narrow beam of α -particles (positively charged helium ion) from radioactive material towards an extremely thin strip of gold (Fig.4.14), and determined the subsequent path of the particles (Fig. 4.15).

A fluorescent screen was set up around the foil. He made the following observations :

- (i) Most of the α -particles passed straight through the metal foil to hit the fluorescent screen;
- (ii) Some α -particles were deflected through a small angle from their original paths;
- (iii) A few α -particles were deflected through very large angles; and
- (iv) Very few α -particles actually bounced back in the direction from which they came.

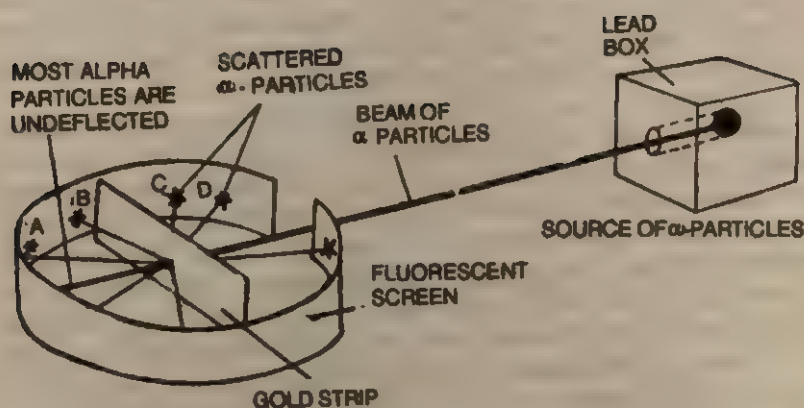


Fig. 4.14 Rutherford's α - particles scattering experiment.

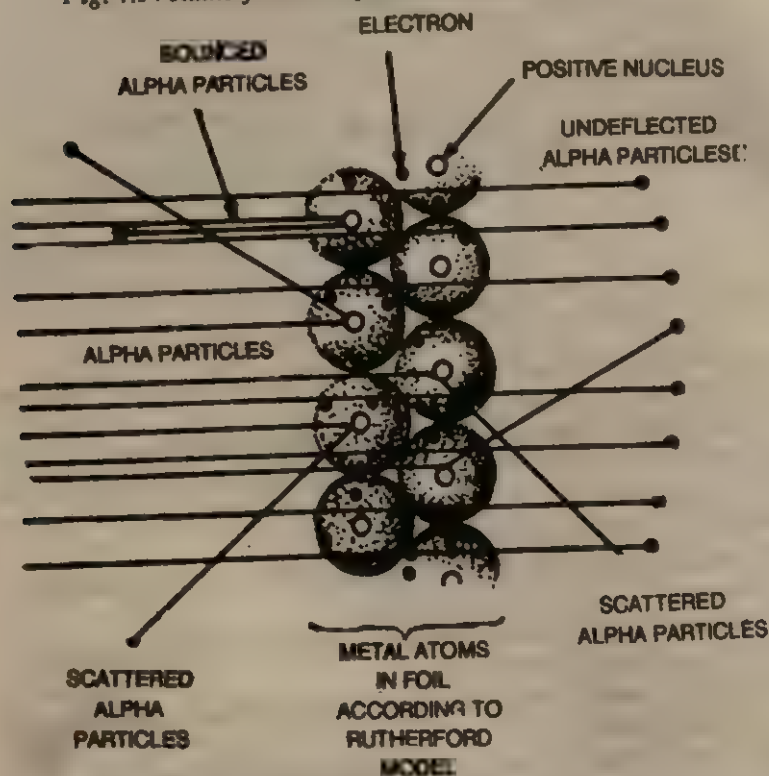


Fig. 4.15: The general pattern of scattering of α - particles by a gold strip made up of atoms

Rutherford reasoned as follows :

Since most of the α -particles pass through the gold strip without experiencing deflection, there seems to be a lot of empty space within an atom.

The angles through which the individual α -group of particles are deflected vary widely. Deflections reveal the following :

- (i) The α -particles are deflected due to collision against the central part of the atom.
- (ii) The central part of the atom is positively charged, hence, the positively charged α -particles are repelled by it.
- (iii) The fact, that very few α -particles are deflected through large angles, shows that the positive charge is contained in a very small space. However, because the kinetic energy of α -particles is very large, only a massive particle with high charge within the metal atom could cause deflection through such large angles.
- (iv) Since the nucleus hold all the atom's positive charge, it also follows ;that the electrons in the atom are distributed outside the nucleus in the remaining volume of the atom.

It is very difficult to imagine how small a nucleus really is? Its diameter is approximately 10^{-15} m compared to the atom itself whose diameter is of the order of 10^{-10} m.

The scattering experiment provided a blow to the Thomson's model as in Thomson's model paricles could be deflected through small angles only. This is because the positive charge in this model is distributed uniformly over the entire volume (Fig.4.16) resulting in a weak field.

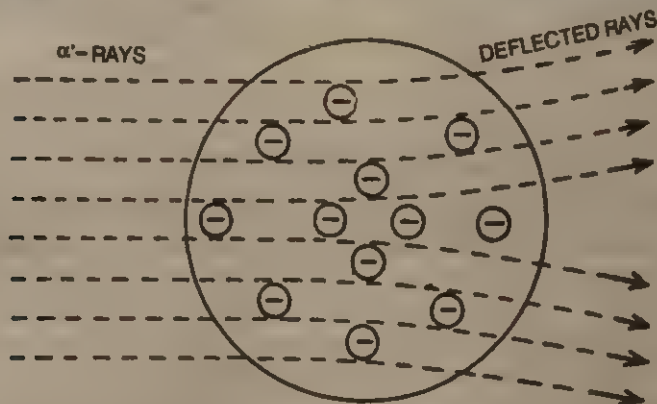


Fig.4.16 Scattering of α -particles on the basis of Thomson's atomic model.

It has been possible to estimate the positive charge on the nucleus by counting the number of α -particles (or number of deflections) scattered in different directions. Thus, it could also be possible that the

charges on different nuclei are always integral multiples of the electron charge but with the opposite sign.

Rutherford, therefore, concluded as follows:

- (i) Mass of an atom and its positive charge are concentrated in a very small region called the nucleus - the atom is mostly 'empty space'.
- (ii) The nuclear charge is balanced by negatively charged electrons revolving round the nucleus.
- (iii) The magnitude of the charge on the massive nucleus is different for different atoms and is nearly one half of the numerical value of the atomic mass.

Rutherford, thus, described that each atom consists of a nucleus (positively charged) around which electrons (negatively charged) are revolving (Fig. 4.17). In the atom of an element the number of electrons is the same as the number of protons in its nucleus. Further to account for the stability of the atom, he suggested that the electrons revolve round the nucleus with high velocities. The centrifugal force so produced counterbalances the coulombic force of attraction between the oppositely charged particles (Fig. 4.17b).

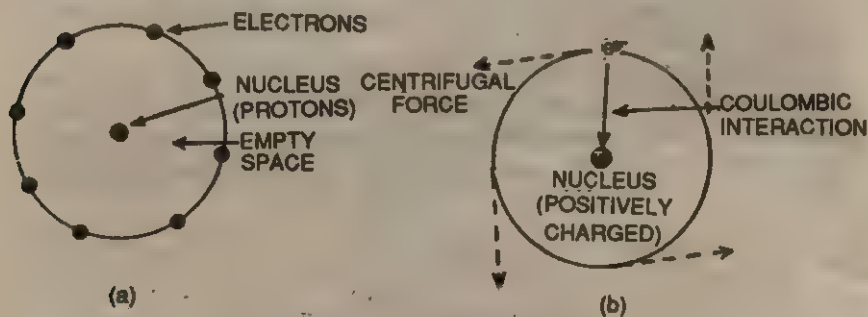


Fig. 4.17 Rutherford's planetary model of the atom.

This was a beautiful model. Its logical simplicity was impressive, since it seemed to be like our solar system (planets move around the sun). However, the planets and the sun are not electrically charged particles. Figure 4.18 illustrates the various features of the scattering experiment. The concept of the nuclear atom provides a firm support for the observations made in the scattering experiment.

4.2.7 Discovery of Neutron

Rutherford (1920) had suggested that in addition to the two charged particles in an atom, there was the possibility of the presence of a particle of essentially the same mass as that of a proton but without any charge.

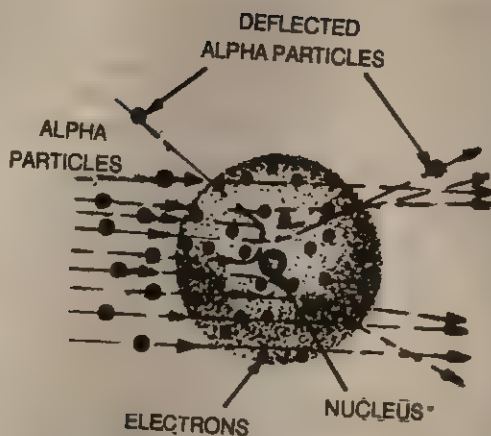


Fig. 4.18 Scattering of α - particles on the basis of Rutherford's nuclear model of the atom.

James Chadwick (1932) showed the existence of neutrons (neutral particles) as well as protons in the nucleus of atoms by bombarding boron, beryllium or lithium metal with α -particles (Fig.4.19). He observed that the radiations emitting from the metal did not experience any deflection in the magnetic field. Hence, Chadwick noted that these radiations must consist of particles that did not possess any electrical charge. On allowing these radiations to strike a block of paraffin

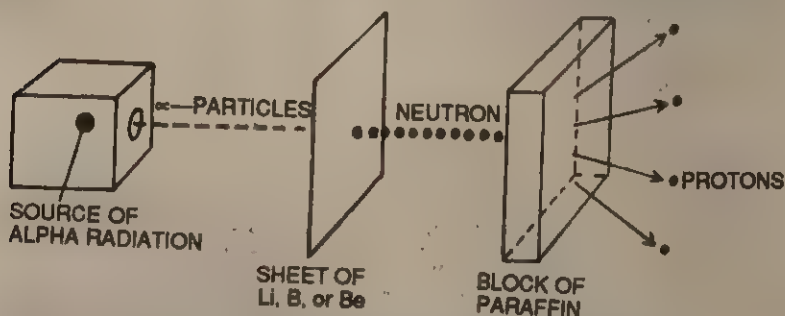


Fig. 4.19 An assembly to produce neutrons.

placed in their path, protons were ejected from the paraffin. The particles in this new form of radiation were able to collide with hydrogen atoms (paraffin contains hydrogen atoms) and cause their ejection by

TABLE 4.3 Properties of atomic particles

Particle	Symbol	Mass	Charge	Location
Electron	e	1/1840 of a hydrogen atom	Negative charge 1.6×10^{-19} coulomb (1 unit)	Revolves round the nucleus
Proton	p	Equal to that of a hydrogen atom	Positive charge; equal and opposite to that of electron (1 unit)	Present in the nucleus
Neutron	n	Equal to that of a hydrogen atom	No charge	Present in the nucleus

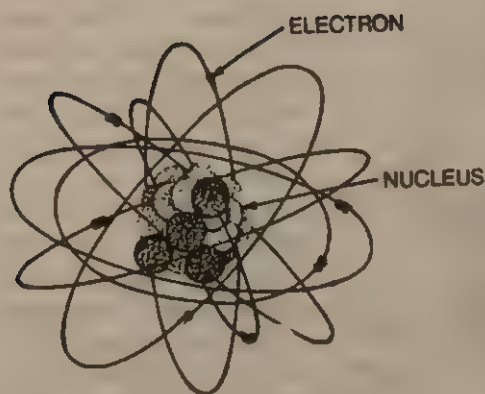


Fig. 4.20 Atoms are composed of protons and neutrons in the nucleus; the electrons are present outside the nucleus.

nucleus which has positive charge and contains most of the mass of the atom. The electrons are present outside the nucleus and occupy most of the volume of the atom. They contribute almost no mass to the atom. Since the number of electrons equals the number of protons, an atom is electrically neutral.

4.3 ATOMIC NUMBER

Rutherford's work established that the mass of an atom and the mass of its nucleus are essentially equal since the mass of electrons is very small. He could not assign a precise positive charge to the nucleus. The magnitude of this charge was found by Henry G.J., Moseley (1913) through experiments with X-ray spectra. From Moseley's relation, it was found that the number of unit positive charges on the nucleus is known as the atomic number of the element. It is denoted by Z . All atoms of a particular element have the same nuclear charge. Moseley investigated the positive charge on the nucleus of atoms of different elements. Since an atom is electrically neutral, the atomic number is also equal to the total number of electrons in the orbits (shells) of an atom of the element. Thus,

$$\text{Atomic number, } Z = p = e$$

Moseley's work thus allows us to state that :

All hydrogen atoms have 1 electron and nuclei having a charge of +1.

All oxygen atoms have 8 electrons and nuclei having a charge +8.

All sodium atoms have 11 electrons and nuclei having a charge +11.

Thus, nuclear charge determines the chemical identity of an atom.

direct collision. Chadwick observed that only a particle similar in mass to the proton could be able to collide with hydrogen atoms. He called these particles, the neutrons. Table 4.3 lists the basic physical properties of the atomic particles.

With the discovery of neutron, the general picture of the atom has emerged as given in Fig. 4.20. Protons and neutrons occupy the small sized

The element to which an atom belongs is, therefore, determined by its number of electrons or its nuclear charge, and not by its mass. Moseley suggested that atomic number was more significant than the relative atomic mass in determining the properties of elements and could be the basis of classifying elements.

4.3.1 Mass Number

The total number of protons and neutrons contained in the nucleus of an element is called its mass number. It is denoted by A . The mass number is always a whole integer. Thus,

$$\begin{aligned}\text{Mass number, } A &= n + p \\ &= n + Z\end{aligned}$$

Protons and neutrons are collectively known as nucleons. These particles are extremely tightly packed together in the nucleus. The difference of mass number and atomic number equals the neutron number. Thus,

$$A - Z = \text{Number of neutrons}$$

For a hydrogen atom, the mass number is equal to its atomic number because there is no neutron in a hydrogen atom. A helium atom contains 2 protons and 2 neutrons. Therefore, the mass number of helium atom is 4. A particular atom with an atomic number of 17 and a mass number of 35, therefore, contains 17 protons and 18 neutrons in its nucleus and has 17 extra-nuclear electrons.

4.3.2 Isotopes

The mass of an atom is mainly attributed to the masses of protons and neutrons contained in its nucleus (the electrons have negligible mass). Since the relative atomic masses of proton and neutron are virtually equal to one, it would be presumed that all the elements would have their relative atomic masses very close to whole number. But this is true only in a few cases, *e.g.*, helium, oxygen and aluminium. The relative atomic masses of helium, oxygen and aluminium are 4.0026, 15.999 and 26.982 respectively. The relative atomic masses of other elements are far from whole numbers, *e.g.*, neon (20.183), magnesium (24.312) and chlorine (35.5). Now the question arises as to why the relative atomic masses of some of the elements are not close to whole numbers? In nineteenth century chemists were able to determine relatively accurate atomic weights for all the elements.

Now take the case of chlorine for which the determined atomic mass is 35.5. The atomic mass of chlorine due to 17 protons and 18 neutrons is $(17 \times 1.0 + 18 \times 1.0)$ 35. The explanation of this difference and the answer to the question raised earlier has been given by considering the existence of isotopes. Naturally occurring chlorine consists of two isotopes, one represented by ${}^{35}_{17}\text{Cl}$ (75%), and the other by ${}^{37}_{17}\text{Cl}$ (25%).

The average atomic mass of chlorine is

$$35 \times \frac{75}{100} + 37 \times \frac{25}{100} = 26.25 + 9.25 = 35.5$$

In 1911, F.W. Aston also showed that atoms of some naturally occurring elements have slightly different masses. Thus, atoms of the same element that possess different masses are called the isotopes of the element. Isotope is a Greek word. 'Iso' is for same and 'tope' is for place. Therefore, the isotopes of an element occupy the same place in the periodic table. **Isotopes have the same number of protons (or same atomic number) but different number of neutrons (or different mass number) in their nuclei.**

As the isotopes of any element have the same number of protons, they should also have the equal number of electrons. Therefore, they show similar chemical properties because these depend upon the electronic configuration of the atom. Neutrons have little influence on the chemical properties of elements. They contribute to the mass of the atom and are responsible for the existence of isotopes.

Isotopes have different physical properties such as densities, melting and boiling points and some other physical properties. This is because of the fact that isotopes contain different number of neutrons in their nuclei.

4.4 ELECTRONIC STRUCTURE OF ATOMS

Rutherford had determined that most of the mass of an atom and all of its positive charge are located in its tiny nucleus in the centre of the atom, surrounded by enough electrons to make the atom electrically neutral. This model of atomic structure is able to explain some properties of the elements - the existence of isotopes - but it still does not explain their chemical and physical properties.

When atoms react with each other, it is only their outer cores that ever come in contact. Their nuclei never come close to each other. Therefore, since it is the electrons that make up most of the volume of the atom, chemical similarities and differences must somehow be related to the way that the electrons are arranged. This arrangement of electrons is called the atom's electronic structure. It will be appropriate to take a stock of the informations and experimental facts that helped to answer this question of electronic structure and led ultimately to our currently accepted theory. A theory called 'Quantum Mechanics' was developed to account for the behaviour of electrons and other small particles. Quantum mechanics had its origins in attempts to explain the nature of light and its interaction with matter.

4.4.1 The Nature of Light

For thousand of years philosophers and scientists have debated the

nature of light. Issac Newton (1642-1727) proposed that light has a **corpuscular or particle nature**, *i.e.*, that it consists of a stream of energetic particles. Dutch physicist Christian Huygens (1629-1695) advanced a belief that light consists of **waves of energy**. There was an apparent conflict between the two theories describing the nature of light. However, most scientists supported the Newton's corpuscular theory which explained fairly well all optical phenomena known at that time. The reflection and refraction of light were adequately explained.

New observations made later could not be explained within the framework of particle theory. In particular, the theory failed to explain the value of the velocity of light in water. The experimental value turned out to be smaller than the velocity of light in air. The particle theory also failed to explain the phenomena of interference and diffraction of light discovered by Thomas Young.

At the beginning of the 19th century, the Huygens wave theory of light received a wide recognition. The wave theory proved to be essential in accounting for interference and diffraction. The wave theory was further developed and perfected by Young and Fresnel. Thus, the wave concept became firmly established.

The most striking effect of light that is not in accord with the wave concept is the photoelectric effect discovered in 1888 by Heinrich Hertz. However, to explain the photoelectric effect using the quantum theory, Einstein was required to think of photons of light as if they were particles. Thus, there emerged the idea that light has a **dual character**, *i.e.*, light has wave properties as well as corpuscular properties.

Light is a kind of electromagnetic wave

In 1879, Maxwell demonstrated that light, magnetism, and electricity are related quantitatively. He further showed that oscillating electrical charges emit electromagnetic radiations as they lose energy. **Light is, thus, a kind of radiant energy or electromagnetic radiation** (radiant energy is classically considered to be a wave phenomenon). Thus, the mechanistic wave theory of light was replaced by the electromagnetic wave theory.

Maxwell showed that all the then known properties of light could be accounted for with the help of energy relations based on the electromagnetic wave nature of light.

The maxwell wave theory of light, considering radiation as a continuous process, also failed to explain some optical phenomena. It was later supplemented by the **quantum theory of light**, according to which the energy of a light wave is emitted in certain packets, *viz.*, quanta or photons which depend on the length of the light wave. Thus, according to modern ideas, light has wave properties as well as corpuscular properties.

Electromagnetic waves and spectrum

The word "electromagnetic" originates from the fact that the wave has electric and magnetic field components that oscillate in direction perpendicular to each other and perpendicular to the direction in which the wave is travelling (Fig. 4.21).

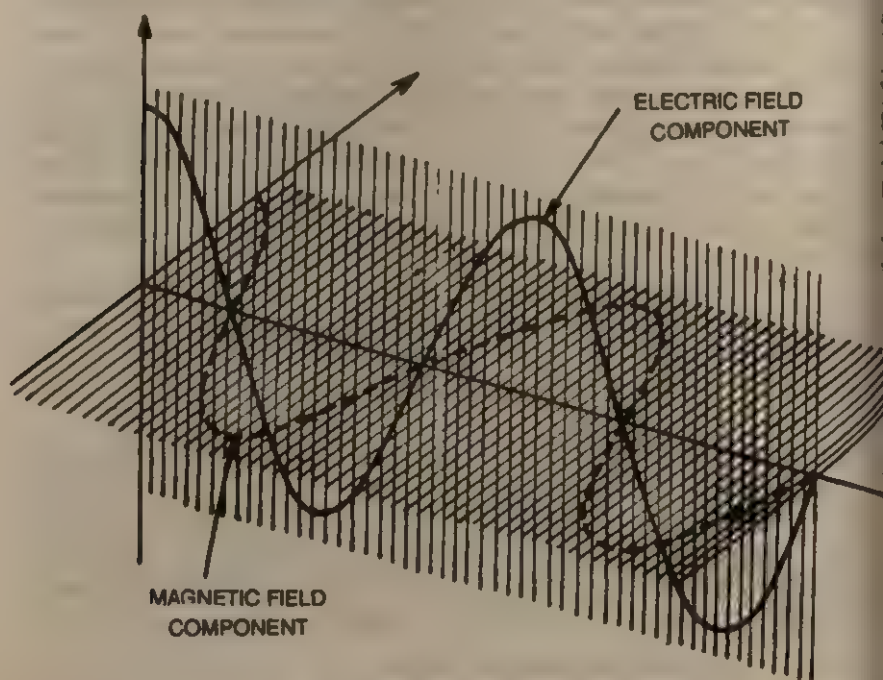


Fig. 4.21 Electromagnetic waves.

Unlike matter waves, light waves (electromagnetic radiations) require no medium for propagation. Light can travel through vacuum or empty space. In vacuum all electromagnetic radiations regardless of wide variations in their wave lengths and frequencies, move with a velocity of $3.0 \times 10^8 \text{ ms}^{-1}$ (experimentally determined). Since ordinary light is a form of electromagnetic radiation, this distinctive velocity is often called the speed of light and is usually given the symbol, c . The arranged entire scheme of different types of radiations in order of increasing wave lengths (or decreasing frequencies) is called the electromagnetic spectrum (Fig. 4.22). A small region lying between 3.8×10^5 – $7.6 \times 10^5 \text{ \AA}$ ($1 \text{ \AA} = 10^{-10} \text{ m}$) of wave length represents visible light. Different regions of the spectrum are given different names e.g., radio frequency region (around 10^6 Hz), used for broadcasting; microwave region (around 10^{10} Hz) used for radar; infrared region (around 10^{13} Hz) a region for heat radiations; ultraviolet region (around 10^{16} Hz) a

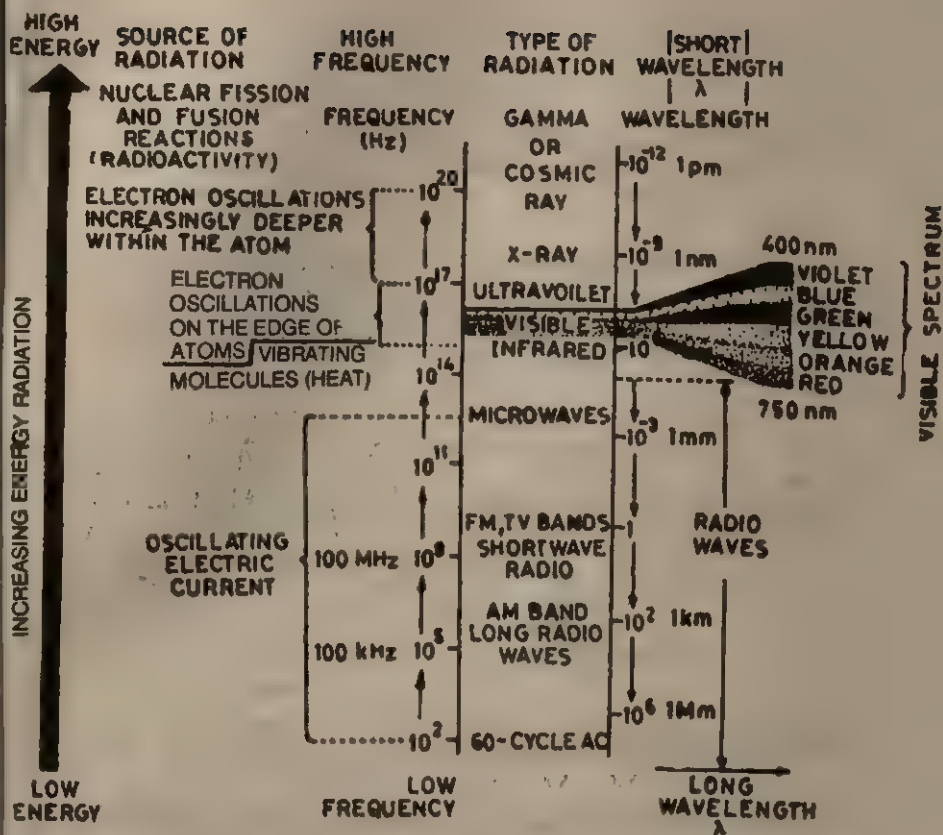


Fig. 4.22 : Electromagnetic spectrum, i.e., a complete range of electromagnetic waves; expanded region of visible radiation.

component of sun's radiation : X-rays (around 10^{19} Hz) and visible region (around 10^{15} Hz. Our eyes can detect only the visible region of the complete electromagnetic spectrum. Special instruments are necessary to detect all other types of radiations.

Characteristics of waves

Some characteristics of waves are illustrated in Fig. 4.23. Waves are variations within some medium such that there is a displacement or disturbance of the medium which increases and decreases in a periodic manner.

There are five characteristic properties associated with any kind of wave, i.e. wavelength, frequency, wavenumber, velocity and amplitude.

(i) **Wavelength** : It is the distance between any two successive crests (or troughs), i.e., "points of equal displacement on successive waves." It

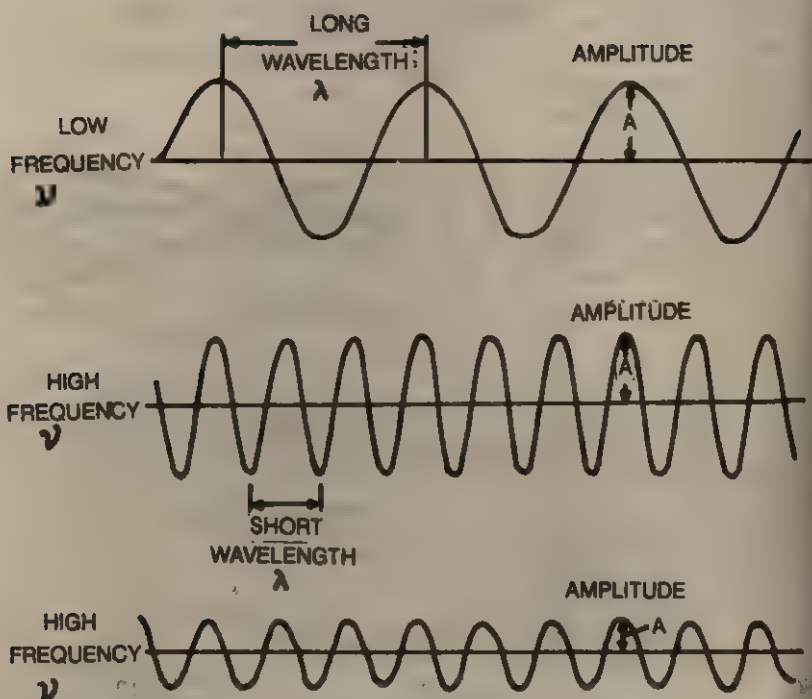


Fig. 4.23 Characteristics of waves. Any wave can be described by its wave length, frequency, amplitude, and speed ($c = \lambda \nu$). The energy of a wave is conveyed by its amplitude.

is usually designated by the Greek letter lambda, λ and is measured in terms of Angstrom units ($\text{\AA} = 10^{-10}\text{m}$) or nanometre, nm ($1\text{ nm} = 10^{-9}\text{m}$).

(ii) **Frequency** : It is the number of complete cycles (waves) or wave crests that pass a given point in 1 second. It is usually represented as cycles per second (cps), i.e., second^{-1} which is given the special name hertz (Hz),

$$1\text{ Hz} \approx 1\text{ s}^{-1}$$

A frequency of 20 Hz means that 20 wave crests pass a given point in 1 s. It is designated by the Greek letter nu, ν . If there are ν waves per second that pass a given point and if the length of each wave is λ , the distance travelled by the wave in 1 s is $\nu\lambda$. This distance travelled is the velocity (or speed) of wave, v

$$v = \lambda \nu$$

(iii) **Velocity** : The distance travelled by the wave front in one second is called its velocity (v).

Since light and all other types of electromagnetic radiations have

a velocity of $3.00 \times 10^8 \text{ ms}^{-1}$ in vacuum ; this velocity is given the symbol, c ,

$$c = \lambda \nu = 3.00 \times 10^8 \text{ ms}^{-1}$$

(iv) **Amplitude** : It is the height of a crest or the depth of a trough. It is designated by the letter, A . The energy per unit volume stored in a wave is proportional to A^2 . For light, the intensity or brightness is proportional to A^2 .

(v) **Wavenumber** : It is the number of wave crests traversed per unit length. It is designated by $\bar{\nu}$. It is expressed in units of reciprocal centimetres, $1/\text{cm}$ or cm^{-1} . It is the reciprocal of wavelength, i.e.,

$$\bar{\nu} = \frac{1}{\lambda}$$

Exercise 4.1 All India radio, Delhi broadcasts at a frequency of 14.2 MHz (magahertz). What is the wavelength of the radio waves emitted by the transmitter.

Solution : The wavelength $\lambda = \frac{c}{\nu}$

$$c = 3.00 \times 10^8 \text{ ms}^{-1}$$

$$\nu = 14.2 \times 10^6 \text{ Hz or } 14.2 \times 10^6 \text{ s}^{-1} \text{ (mega means } \times 10^6)$$

Substituting these values, we have

$$\frac{3.00 \times 10^8 \text{ ms}^{-1}}{14.2 \times 10^6 \text{ s}^{-1}} = 21.1 \text{ m}$$

Exercise 4.2 What is the wavelength of the various types of light having frequency as shown against each other,

$$\text{Green light's } \nu = 6.67 \times 10^{14} \text{ Hz}$$

$$\text{Violet light's } \nu = 7.31 \times 10^{14} \text{ Hz}$$

$$\text{Red light's } \nu = 4.57 \times 10^{14} \text{ Hz}$$

Solution : Since frequency and wavelength are inversely proportional to each other $\lambda = c/\nu$

Substituting the value of c and ν , we get,

$$\text{Green light } \lambda = \frac{3 \times 10^8 \text{ ms}^{-1}}{6.67 \times 10^{14} \text{ s}^{-1}} = 4.50 \times 10^{-7} \text{ m}$$

$$\text{Violet light } \lambda = \frac{3 \times 10^8 \times \text{ms}^{-1}}{7.31 \times 10^{14} \text{ s}^{-1}} = 4.1 \times 10^{-7} \text{ m}$$

$$\text{Red light } \lambda = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{4.57 \times 10^{14} \text{ s}^{-1}} = 6.56 \times 10^{-7} \text{ m}$$

Exercise 4.3 What is the frequency of visible region extending from violet (400 nm) to red (750 nm).

Solution : Since $1 \text{ nm} = 10^{-9} \text{ m}$

$$\text{Frequency of violet light } \nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ ms}^{-1}}{400 \times 10^{-9} \text{ m}} = 7.5 \times 10^{14} \text{ s}^{-1}$$

$$\text{Frequency of red light } \nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ ms}^{-1}}{750 \times 10^{-9} \text{ m}} = 4.0 \times 10^{14} \text{ s}^{-1}$$

4.4.2 Light and Energy

Light is a form of energy. Sun light is a big source of solar energy. This energy has been utilized for various purposes. During winter, we always love to sit in the sun. How much energy is carried by light ? The answer to this question found its origin in the work of Max Planck (1900) and Albert Einstein (1905). They proposed that a beam of light consists of small bundles of energy called light quanta or photons, and that the energy, E , of a photon is proportional to its frequency,

$$E = h\nu$$

where h is a constant, called the Planck's constant. The value of h is 6.63×10^{-34} Js or 3.99×10^{-13} kJs mol $^{-1}$.

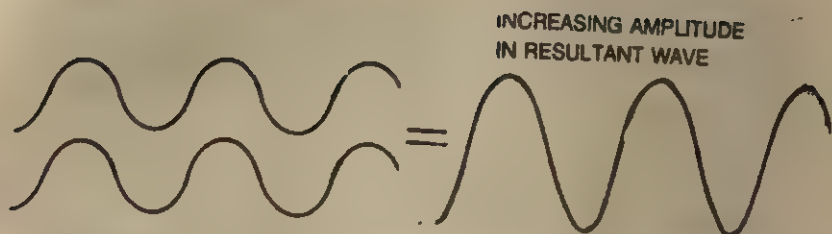
This expression holds good for all forms of electromagnetic radiations. The description of light in terms of photons amounts to saying that light has a corpuscular (particle) character.

4.4.3 Interference and Diffraction

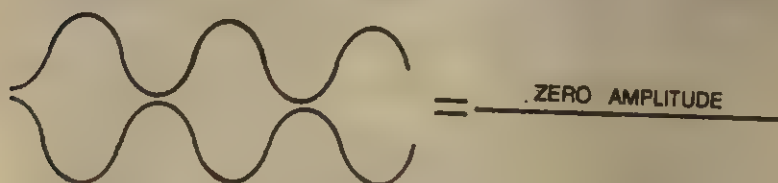
Light is an electromagnetic wave and it behaves like any other wave, e.g., waves on water surface. If waves are generated at two points close together the waves spreading out from these points interfere with each other and produce an interference pattern. In general, the two waves travel a different distance to reach the same point. In traversing the distance, the crests of the two waves line up and arrive together, at some points, producing a wave of larger amplitude. At other points, the crests of one wave and the troughs of the other will arrive. The two waves cancel and produce a zero amplitude at that point (Fig. 4.24). When light is passed through two very small openings (slits) that are very close together, an interference pattern with a series of alternately bright and dark spots (or lines) is obtained on a screen placed behind the partition with openings (Fig. 4.25)

When waves come across some obstacle in their path, they bend. This property is known as diffraction. Thus, light waves passing through opening tend to bend around its edges and spread out as they emerge through the opening. The magnitude of this diffraction depends on the wavelength of the waves and the size of the hole. If the size of hole for light is small compared with the wavelength of the light, a blurred image composed of light and dark areas is produced. This image is diffraction pattern. Similar diffraction patterns can be produced with certain particles, including electrons, protons and neutrons. Since diffraction can only be explained as a property of waves this confirms the wave nature of matter.

Because diffraction and interference patterns are produced only by openings, slits and other obstacles (or objects) comparable in size to the wave length of light they are not readily observed. Light produces



(A) TWO WAVES IN PHASE LEADING TO CONSTRUCTIVE INTERFERENCE



(B) TWO WAVES OUT OF PHASE LEADING TO DESTRUCTIVE INTERFERENCE

Fig. 4.24 Constructive and destructive interference

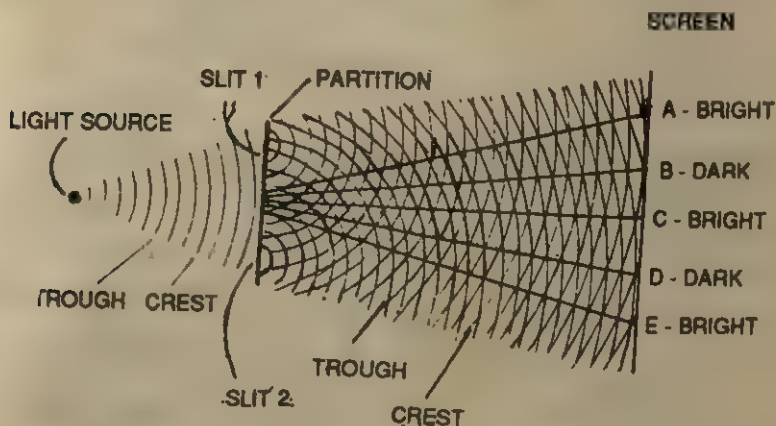


Fig. 4.25 The interference pattern of two sets of waves of the same wavelength. Identical waves from two holes interact in phase and out of phase producing the alternating pattern of bright and dark areas.

Because diffraction and interference patterns are produced only by openings, slits and other obstacles (or objects) comparable in size to the wave length of light they are not readily observed. Light produces sharp images of objects of ordinary size. It, therefore, appears to travel in straight lines like a beam of particles.

4.4.4 Photoelectric Effect and the Particle Nature of Light

When a beam of light is allowed to fall on a metallic surface, electrons are emitted from the surface. These electrons can set up an electric current (Fig. 4.26). This phenomenon is known as the **photoelectric effect**, and the emitted electrons are called **photoelectrons**. The following observations are shown by the experiments.

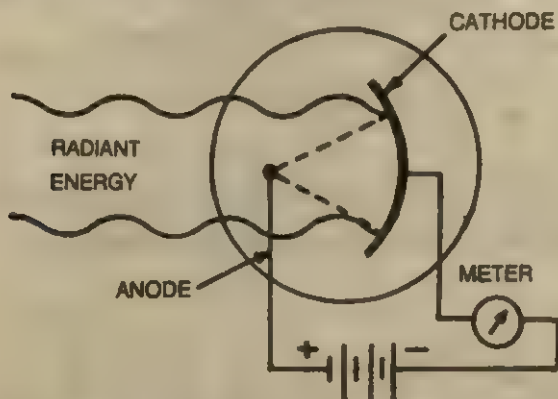


Fig. 4.26 Detecting the photoelectric effect. Radiation of sufficient energy causes the emission of photoelectrons from the cathode. The photoelectrons ejected from the irradiated plate are attracted by the anode which finally get attached to it, completing the electric circuit and allowing current to flow.

1. For each metal there is a frequency of light, ν_0 i.e., the critical frequency, below which no electrons are emitted.
2. At frequencies, ν greater than ν_0 the kinetic energy of the emitted electrons is proportional to $\nu - \nu_0$.
3. The number of electrons emitted per second (current) is proportional to the intensity of light, but is independent of the frequency so long as it is above the critical value stated in 1 above.
4. The number of electrons emitted is also independent of the energy of light.
5. The kinetic energy of the electrons is independent of the intensity of light, but depends upon on the frequency (or wavelength)
6. Electrons are emitted from the surface almost instantaneously (less than 10^{-9} s after the surface is illuminated), even with very low-intensity light.

These observations could not be explained by the wave theory of light. According to classical theory, electrons should accumulate energy and should be released when they have enough energy to get away from the metal atoms. Thus, if light is made more energetic, then the current should increase even though the light intensity remains constant. The answer to these observations was given by Albert Einstein in 1905; the light behaves as though it consists of particles, given the name photons.

Each photon has energy which it can transfer to a single electron during collision and disappears from existence. The electron may then have sufficient energy to escape from the metal. A part of its energy is used to overcome the attractive forces which keep the electron bound to the metal and the remaining energy appears as the kinetic energy of the emitted electron.

$$\begin{aligned} \text{Energy of photon} &= \text{Energy needed to} & + & \text{Kinetic energy of} \\ &\text{overcome the attractive} & & \text{emitted electrons} \\ &\text{forces on the electron} & & \\ \text{or } h\nu &= W + KE \end{aligned}$$

4.4.5 Atomic Spectra

A beam of white light on passing through the prism emerges as a spectrum containing all the wavelengths on the screen (Fig.4.27). The dispersion of the light through the prism is observed on the screen as a continuous spectrum displaying a gradual blending of colours from red through orange, yellow, green, blue and indigo to violet.

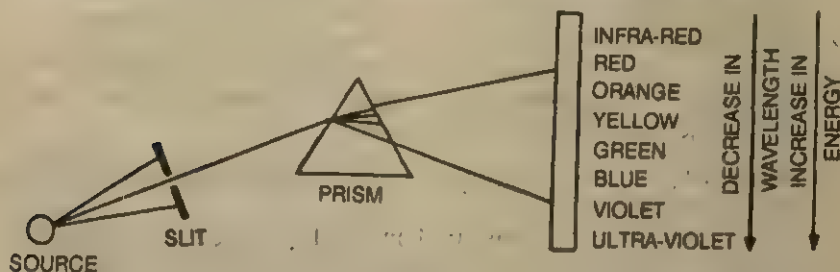


Fig. 4.27 Dispersion of white light, such as sunlight by a prism- production of a continuous band of its constituent wave lengths, which we perceive as a band of colours. Colours correspond to light of different wavelengths and different energies.

If the source consists of atoms of an element such as hydrogen or sodium (from a gas discharge tube) the entire pattern projected on the screen is quite different from that obtained with white light. In the case of hydrogen the observed spectrum consists of a number of discrete lines projected on the screen [(Fig. 4.28 (a)]. Figure 4.28 (b) shows some lines in the visible region of the spectrum. Obviously, the visible

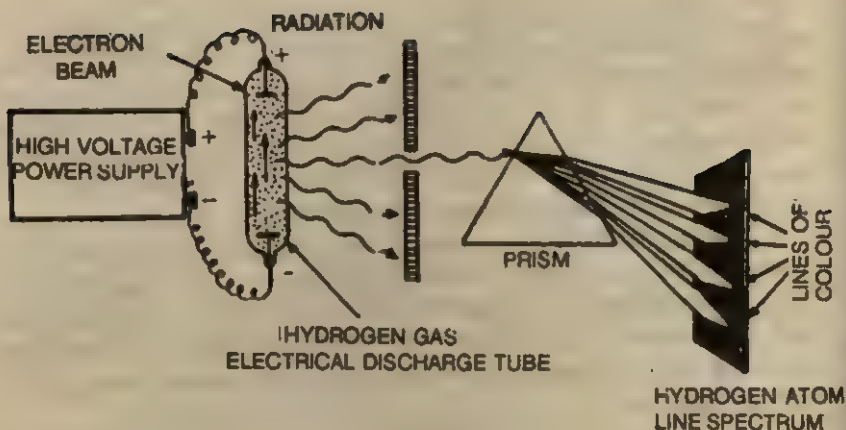


Fig. 4.28(a) Production of hydrogen spectrum

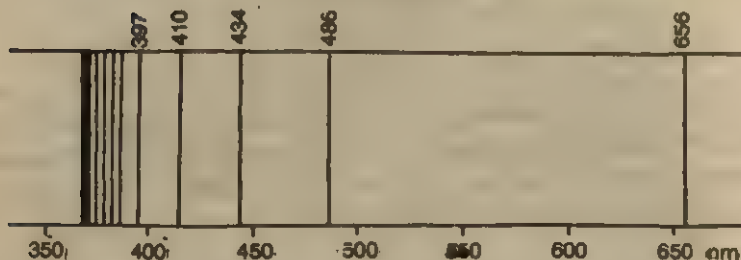


Fig. 4.28(b) Visible portion of the spectrum of hydrogen. The Balmer series of lines in the hydrogen emission spectrum

light emitted by hydrogen does not contain radiations of all wavelengths, as sunlight does.

A study of many elements shows that the spectrum of each element is unique and serves as a mean of identifying the element. Although each is unique, the spectra of various elements do exhibit some similarities. Also there are certain regularities in the features of any one spectrum.

An atom or ion on absorbing energy (heat energy or electrical energy) becomes unstable and tends to release all or a part of the excess energy in the form of ultraviolet or visible light. Energizing the electrons in an atom corresponds to increasing their distance from the nucleus, and in this state (absorption of energy) the atom is described as excited. The atom rapidly acquires its original state, the ground state (a state in which the electrons possess the lowest energy). In its transition from the excited state to ground state, the atom (electron) releases the

energy (electromagnetic radiation) absorbed, which on refraction gives a spectrum characteristic of the atomic species. Such a spectrum is known as an atomic spectrum. It is evident that if there is no restriction on the energy absorbed, the emitted light will result into a continuous spectrum.

Around 1860, Robert Bunsen and Gustav Kirchhoff built a spectroscope to spread out the light emitted by elements as they were heated in flame. With their spectroscope, they found that the light emitted was not composed of a continuous band of colours as is white light but contained only certain wave lengths (line spectrum). The emission spectrum of various elements was found to have a characteristic set of lines, so line spectra come to serve as 'finger prints' for the identification of elements. Rubidium, caesium, and a number of previously unknown elements were discovered between 1868 - 1880 through the observation of their spectral lines. Alkali metals like, Li, Na and K and alkaline metals like, Ca, Sr and Ba are detected in qualitative analysis by flame test.

The study of atomic spectra has been helpful in elucidating the nature of electron behaviour in atoms. Atomic spectrum is sometimes called line spectrum as it is composed of a series of bright lines at a few distinct wavelengths and total darkness everywhere else. Each line corresponds to a definite frequency. The frequency of the radiation emitted from an atom is a quantitative measure of the energy change experienced by an electron in that atom. The relation between energy and frequency is given by the Planck's expression ($E = h\nu$). Atomic spectrum is also called emission spectrum since it relates to light emitted from atoms. The opposite is an absorption spectrum, obtained if white light (light of all visible wavelengths) is passed through a substance. Black lines are seen where light of some wavelengths has been absorbed by the substance. This spectrum is clearly related to the emission spectrum. On examining the spectrum of sunlight certain dark lines did not correspond to the absorption spectrum of any element then known on the earth (1868). The element was therefore called helium after the Greek *helios*, the sun. Helium was, of course later discovered on the earth by Ramsay in 1895 (after 27 years).

The hydrogen atom gives the simplest pattern of lines. Figure 4.28(b) shows the lines which appear in the visible region of the spectrum. Some more lines can also be seen in the infrared and ultraviolet regions. In 1885, Balmer showed that the wavelengths of all the lines in the visible spectrum of hydrogen could be related by an equation in the form,

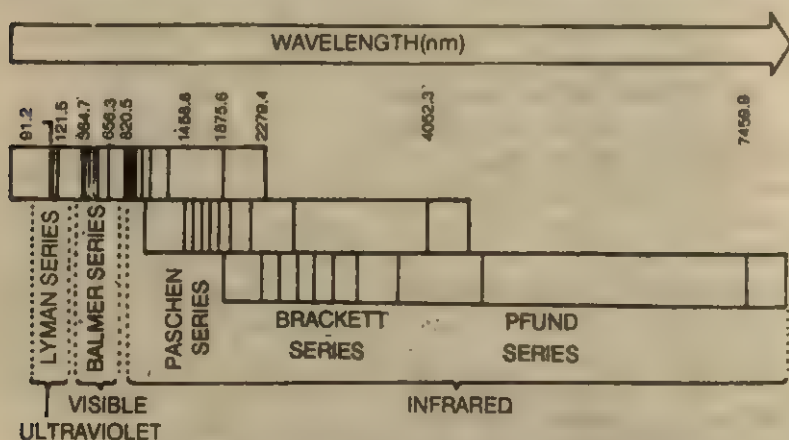
$$\frac{1}{\lambda} = \bar{\nu} \text{ (cm}^{-1}\text{)} = \text{Constant} \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

where λ is the wavelength and n is a whole number that can have values equal to or greater than 3 (3, 4, 5, 6,and so on). Thus, when $n = 3$, $\lambda = 656.475$ nm. Similarly when $n = 4, 5$ and 6 we compute λ to be 486.3, 434.2 and 410.3 nm respectively. The constant is the *Rydberg constant* (R) which has a value $109677.581 \text{ cm}^{-1}$

All of the lines related by the above expression constitute **Balmer series**. Other series of the lines were also observed in the atomic spectrum of hydrogen and the wavelengths of the lines within each series can be found by the **Rydberg equation**.

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (\text{where } n_2 > n_1)$$

Where n_1 and n_2 are integers that may assume values of 1, 2, 3 ... ∞ with the requirements that n_2 is always greater than n_1 . Thus, when $n_1 = 1$ the value of the n_2 can be 2, 3, 4, and the series is known as the **Lyman series** and it is located in the ultraviolet region of the electromagnetic spectrum. This and other series are summarized in Fig. 4.29 and Table 4.5.



$$\frac{1}{\lambda} = 109677 \text{ cm}^{-1} \cdot \frac{1}{2^2} - \frac{1}{3^2}$$

$$\frac{1}{\lambda} = 109677 \cdot \frac{5}{36} \text{ cm}^{-1}$$

Taking the reciprocal gives

$$\lambda = \frac{36}{5 \times 109677} = 656 \text{ nm} \quad (1 \text{ nm} = 10^{-9} \text{ m})$$

TABLE 4.5 Series of lines in the hydrogen spectrum

Series	n_1	n_2	Spectral region
Lyman	1	2,3,4,.....	Ultraviolet
Balmer	2	3,4,5,.....	Visible
Paschen	3	4,5,6,.....	Infrared
Brackett	4	5,6,7,.....	Far infrared
Pfund	5	6,7,8,.....	Far infrared

4.4.6 Atomic Spectra and Rutherford's Model

Rutherford's X-ray scattering experiments provided the concept of a nuclear atom, according to which an atom consists of a heavy positively charged nucleus surrounded by lighter negatively charged electrons, which occupy most of the volume. This model seemed to be perfectly analogous to the relationship between the sun and the planets of our solar system. Further, the coulombic force of attraction ($q_1, q_2/r^2$) between the oppositely charged particles (electron and proton) is mathematically similar to the gravitational force, ($Gm_1, m_2/r^2$) between a planet and the sun. According to Newtonian theory, planets describe well defined orbits around the sun which persist forever. It could also help in calculating the trajectory of the planets which are well in agreement with experimental measurements. Accordingly, electrons in the planetary model of the atom should move around the nucleus in well defined calculable orbits. A body pursuing a circular path gets accelerated because of changing direction constantly. Similarly an electron is accelerated. Maxwell's electromagnetic theory showed that accelerated (oscillating) charged particles lose energy continuously in the form of radiations. However, the planets and the sun are not electrically charged, hence, they continue to move without losing any energy.

Thus, as the electron revolved about the nucleus, it would have to emit energy. The only way in which the electron could compensate for this energy loss would be to make a smaller orbit, i.e., a decrease in orbital radius would have to take place. Thus, with the continuous loss of energy, the orbital radius would continue to decrease until the electron spirals into the nucleus (Fig. 4.30). In the process, orbiting electron emits radiation continuously portraying a continuous spectrum contrary to the observed line spectrum. This view of the orbiting electron challenges the stability of the atom. However, the atom, in a manner char-

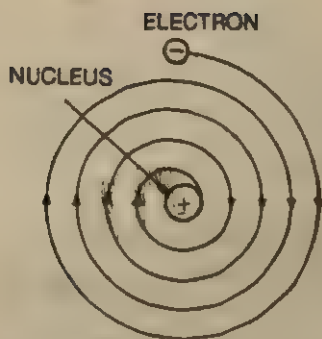


Fig. 4.30: Electron orbiting constantly around the nucleus. The collapse of the Rutherford's atom. As it travels around the nucleus, the electron radiates energy and approaches the nucleus in a spiral path.

regarding the positions of electrons relative to each other and to the nucleus or to their state of motion around the positively charged nucleus.

To circumvent the objections levelled against the Rutherford's atomic model, Niels Bohr in 1913 put forward his theory regarding the structure of atom. He retained the main features of the nuclear model and proposed some modifications. He incorporated quantum arguments to account for line spectra of the elements. The proposed model is known as Bohr's model. To keep the clarity in understanding the atomic models, the hydrogen atom (H), with a proton as the nucleus and one associated electron, will be used. In this system, the proton is assumed to be stationary with regard to any motion the electron might have (in view of the relative masses of the proton and the electron). The hydrogen atom is the simplest.

In the advancement of Bohr's model the following postulates were made,

1. Electron can move around the nucleus in certain circular orbits (known as energy levels) only without emitting electromagnetic radiations.

These energy levels starting from the one close to nucleus, are numbered as 1, 2, 3, 4, etc. or designated as K, L, M, N, etc. (Fig. 4.31). Each energy level is associated with a fixed amount of energy. These energy levels are also called allowed or stationary states because the energy of the electron remains constant as long as it keeps residing in the same energy level. Thus, it does not lose energy and fall into the nucleus. The rungs (or arms) of a ladder are analogous to fixed energy levels of electrons in their paths around the nucleus. The lowest rung

characteristic of all matter does not tend toward self-destruction. Obviously, some more modifications were required to solve the puzzle.

4.4.7 Bohr's Model of the Hydrogen Atom—A Particle Model

Rutherford's atomic model provides a reasonable view of the atom but it does not convey

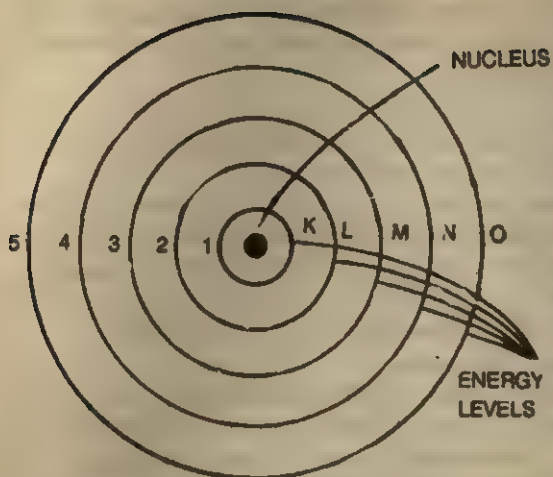


Fig. 4.31 Bohr's model of an atom.

energy level to the next one, an electron must gain/lose just the right amount of energy. (Fig. 4.32).

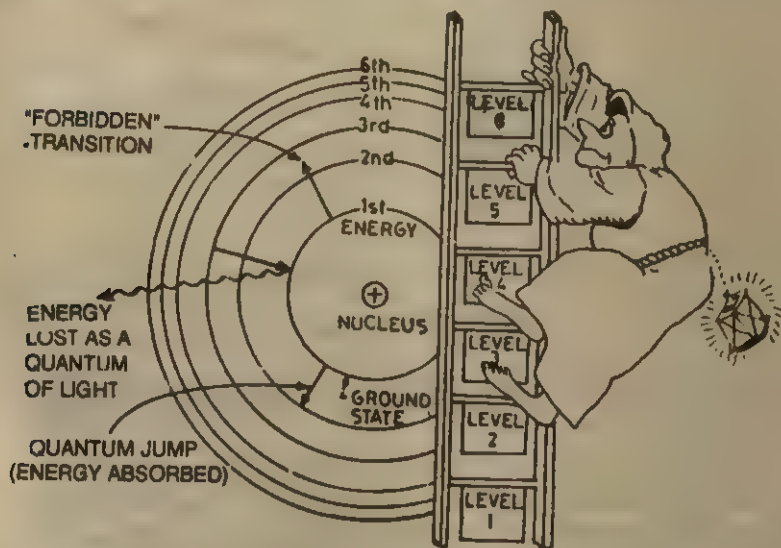


Fig. 4.32 The energy levels in a Bohr's atom are similar to the rungs fixed on a ladder

2. An electron neither loses nor gains energy if it keeps moving in one of these stationary states.

An electron in the lower/higher lying level may be transferred to a

higher/lower energy level by absorption/emission of a quantum of energy ($h\nu$) equal to the energy difference between the two levels whose frequency, ν , is given by the relation,

$$\Delta E = E_i - E_f = h\nu \dots\dots\dots(4.1)$$

where h is Planck's constant and E_i and E_f are the initial and final values of the energy of the electron respectively.

3. The only orbits in which an electron can travel are those in which the angular momentum of the electron be an integral multiple of $h/2\pi$. As long as the electron remains in such orbits, it does not radiate energy.

Therefore, $mvr = nh/2\pi \dots\dots\dots(4.2)$

where n , an integer = 1, 2, 3 and so on.

Significance of Bohr's Postulates

Rutherford considered that electron could occupy any orbit around the nucleus, while Bohr suggested that electron could move in certain circular orbits (stationary states) only in which an electron can reside without the emission of radiant energy.

It was to account for atomic spectra that Bohr suggested that an electron moves in circular orbits round the nucleus. A set of possible energy levels of the hydrogen atom that could rise to the observed spectrum is shown in Figs. 4.33 (a) and 4.33 (b).

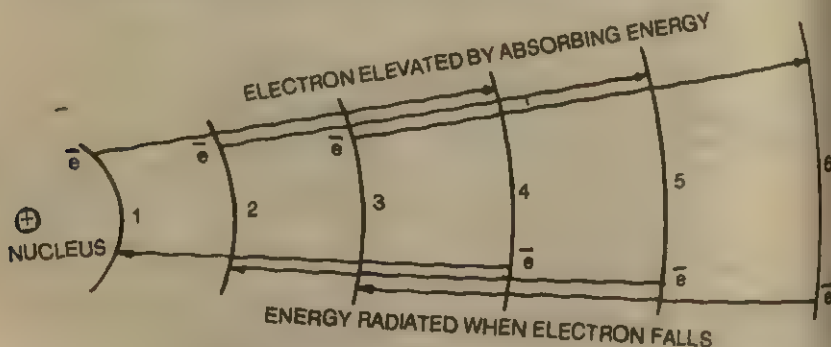


Fig. 4.33 (a) Permitted electron orbits of Bohr's atom; Electron transitions which give rise to atomic spectra.

Bohr assumed in his 2nd postulate that each line observed in the spectrum of an element results from the passage of an electron from an allowed orbit with energy E_i to one of lower energy E_f and that this difference in energy is emitted as a quantum of radiation of frequency ν in line with the equation (4.1). If E_i is greater than E_f , energy is radiated and if E_i is less than E_f , energy is absorbed by the atom. The former corresponds to emission of energy, the latter to absorption of energy. The energy of atomic system is said to be quantized because only certain energies are allowed. Accordingly, E_i and E_f have distinct values.

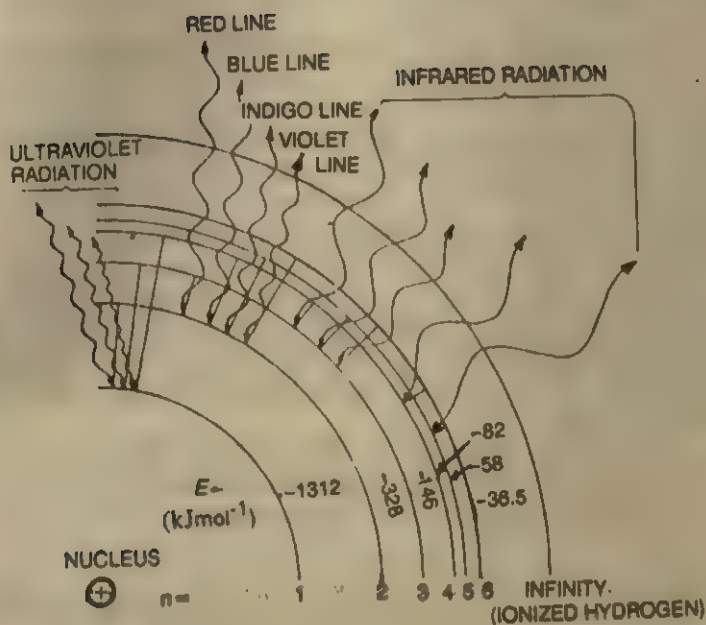


Fig. 4.33 (b) Energy level diagram of hydrogen atom

Then the situation permits the frequency, ν to have distinct value as well. Thus, an atom can be characterized by its energies and the emitted frequencies.

The third assumption amounts to a quantization of the angular momentum and all the physical variables (such as energy, radius, etc), related to it by the usual definitions. He assumed that the hydrogen atom spectrum could be explained if the electron moved in those planetary orbits that limit the angular momentum to integer multiples of $h/2\pi$.

The energy of the levels in Fig. 4.33 is given by the expression.

$$E_n = - \frac{2\pi^2 m e^4 Z^2}{n^2 h^2}$$

in which m = mass of the electron, e = the value of the charge on the electron, Z = number of charges, h = Planck's constant, n = an integer of value 1,2,3....., and E_n = energy of state n . Since Bohr used quantum theory to propose the existence of allowed states, they are known as quantum states of the atom. The integer ' n ' which determines the energy is called a quantum number.

The energy (E_n) of each stationary state in the hydrogen atom is,

$$E_n = \frac{1312}{n^2} \text{ kJ mol}^{-1}$$

Since the lowest permissible value of the lowest energy level, called the ground state has a value of $-1312 \text{ kJ mol}^{-1}$. The negative sign is used to provide agreement with the convention that potential energy of attraction has a negative value. The negative value depicts a more stable state than one in which the proton and electron are separated by an infinite distance. In other words, the electron in hydrogen atom has less energy, i.e., the atom is more stable. The potential energy is zero when the electron is far removed from the nucleus i.e. when the hydrogen atom is ionized. Thus, to ionize a hydrogen atom a minimum of 1312 kJ of energy is required.

The ionization energy of an isolated gaseous hydrogen atom is, therefore, $1312 \text{ kJ atom}^{-1}$. Bohr's energy expression correctly reproduces the hydrogen line spectrum. This is well illustrated by Exercise 4.5.

Exercise 4.5 (a) Calculate the energy liberated when an electron drops from the 3rd to the 2nd energy level in hydrogen atom.

(b) Also calculate the wavelength of the radiations emitted during transition.

Solution : We have energy levels $n = 2$ and $n = 3$

$$E_2 = -\frac{1312}{4} \text{ kJ mol}^{-1}, H E_3 = -\frac{1312}{9} \text{ kJ mol}^{-1}$$

The energy liberated : $= E_{\text{initial}} - E_{\text{final}}$

$$\begin{aligned} E_3 - E_2 &= -1312 (1/3^2 - 1/2^2) \\ &= -1312 (1/9 - 1/4) \\ &= -182.2 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Energy per atom} &= \frac{182.2}{6.023 \times 10^{23}} \text{ kJ atom}^{-1} \\ &= 3.03 \times 10^{-19} \text{ J atom}^{-1} \end{aligned}$$

This energy refers to the energy carried by one photon. To calculate the wavelength we use Planck's equation, $E = h\nu$

$$E = h\nu$$

$$\text{or } \lambda = \frac{hc}{E} \quad \left(\text{since } \nu = \frac{c}{\lambda} \right)$$

Substituting the value of $h = 6.63 \times 10^{-34} \text{ Js}$ and

$$\begin{aligned}
 v &= 3.00 \times 10^8 \text{ ms}^{-1}, \text{ we get} \\
 &= \frac{6.63 \times 10^{-34} \text{ Js} \times 3.0 \times 10^8 \text{ ms}^{-1}}{3.03 \times 10^{-19} \text{ J}} \\
 &= 6.56 \times 10^{-7} \text{ m} \\
 &= 656 \text{ nm}
 \end{aligned}$$

This value of λ corresponds to the first line in the Balmer series for hydrogen atom.

Accordingly, the fact that the energy of an atom can have only distinct quantities of energy and none in between is phrased by saying that "the energy of the electron is quantized" (i.e., put in one packet). The statement, the electron in an atom can possess only distinct quantities of energy" can be put in other words also, i.e., the electron moves only in certain energy levels in the atom.

By the application of this theory, Bohr was able to calculate the wavelength of the main lines of the spectrum of hydrogen and hydrogen like atoms or ions such as H^+ , Li^{2+} , etc, with a reasonable accuracy, and also the radius of hydrogen atom. It failed to predict the spectra of more complicated atoms. Bohr's ideas were not found adequate to solve the problems of the electronic structure of the atoms.

Exercise 4.6 Calculate the wavelength of radiation and the energy per mole required to ionize a hydrogen atom in the ground state.

Solution : To get the ionized hydrogen, it is necessary to promote the electron to a level that is infinitely high, so $n_1 = \infty$. Using the Rydberg's equation,

$$\frac{1}{\lambda} = -109677 \text{ cm}^{-1} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

In the units of frequency the equation becomes,

$$v = -(3.29 \times 10^{15} \text{ s}^{-1}) \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Substituting for n_1 and n_2 (ground state) we get,

$$v = -(3.29 \times 10^{15} \text{ s}^{-1}) \left(\frac{1}{\infty^2} - \frac{1}{1^2} \right) = 3.29 \times 10^{15}$$

$$\lambda = \frac{c}{v} = + \frac{3.0 \times 10^8 \text{ ms}^{-1}}{3.29 \times 10^{15} \text{ s}^{-1}} = +9.12 \times 10^{-8} \text{ m} = 91 \text{ nm}$$

The radiation is in the far ultraviolet region of the spectrum of hydrogen atom.

$$\begin{aligned}
 \therefore \Delta E &= h v = 6.63 \times 10^{-34} \text{ Js} \times 3.29 \times 10^{15} \text{ s}^{-1} \\
 &= 2.18 \times 10^{-18} \text{ J/atom} \\
 &= 2.18 \times 10^{-10} \text{ J/atom} = 1.313 \times 10^6 \text{ J/mole} \\
 &= 6.023 \times 10^{23} \text{ atom/mole} \\
 &= 1313 \text{ kJ mol}^{-1}
 \end{aligned}$$

The experimental value is 1312 kJ mol^{-1}

Shortcomings of Bohr's Model

The great success of the Bohr's model was in its ability to account for the lines in the hydrogen atom spectrum. It had serious defects for all other atoms which have more than one electron. But still it opened the way to quantum mechanics. In view of the accepted quantum mechanical model of atom, the additional failures of the Bohr's planetary model can be listed as given below :

Even for atoms with one electron, it failed to explain the fine structure (groups of closely spaced lines) of the lines. The fine structure is observed when a single spectral line in the spectrum splits into very closely related lines under a spectroscope of strong resolution. The splitting of a single spectral line into even more closely spaced lines in the presence of magnetic field (the Zeeman effect) could not be explained.

In view of the de Broglie's dual character (wave-like and particle-like) of material particles (electron, proton, atom, *etc.*) the transition of electron from one permitted orbit to another is not adequate.

According to Bohr's theory an electron has a well defined trajectory. Thus, it appears feasible to locate the position of the electron but this is found to be impossible in view of Heisenberg's uncertainty principle according to which it is impossible to measure simultaneously both the exact position and exact velocity of a material particle.

Quantum Mechanical Model of the Atom

The resolution of difficulties encountered with the Bohr's model began in 1924. A French physicist Prince Louis de Broglie suggested that Bohr's integers ($n = 1, 2, 3$) and Planck's wave—particle theory of radiation (light is a form of electromagnetic radiation) could be reconciled if all moving particles (electrons, protons and atoms) were considered to exhibit wave-like motion*. Louis de Broglie on the basis of his mathematical argument proposed that the wavelength associated with a particle of mass, m and the speed, v is,

$$\lambda = \frac{h}{mv} = \frac{h}{p} \quad (\text{Since } mV = \text{momentum} = p)$$

* Most of the phenomena pertaining to light are described in terms of wave nature. A photon of light behaves both like a particle and a wave. Louis de Broglie advanced in 1924 the concept of particle-wave. It turned out that photons follow the two fundamental equations :

$$E = h\nu \quad (\text{Planck's equation}) \dots\dots\dots (1)$$

$$E = mc^2 \quad (\text{Einstein's equation}) \dots\dots\dots (2)$$

$$\text{Combination equations (1) and (2), } mc^2 = h\nu \text{ or } \frac{h\nu}{c} = mc$$

Since $\lambda = \frac{c}{\nu}$ substitute the value of ν in equation (3)

$$\frac{hc}{\lambda c} = mc \text{ or } \frac{h}{\lambda} = mc \text{ or } \lambda = \frac{h}{mc} = \frac{h}{p} \quad (\text{Since } mc = \text{momentum} = p)$$

The above expressions is called the de Broglie equation and it correlates the particle properties such as mass with wave properties such as wavelength. de Broglie assumed the same relationship for the motion of particles such as electron, viz. $\lambda = \frac{h}{mv}$

where v is the velocity

He was led to propose this equation on the basis of Einstein's theory of relativity according to which the momentum of a photon is given by the expression,

$$p = \frac{h}{\lambda}$$

Diffraction pattern produced by passing a beam of fast moving electrons through a crystal provided enough support to the de Broglie's concept. The wavelength of a fast moving electron falls in the X-ray region and is considerably shorter than that of visible light. This fact has been made use of in developing an electron microscope. The ordinary microscope limits the size ($\sim 500\text{nm}$) of the object that can be observed in the visible range only. An object smaller than the wavelength of visible light cannot be observed with clarity as diffraction blurs the image.

However, the electron microscope can distinguish object as small as 0.1 nm because the electron travelling at high speed is much smaller than the wavelength of visible light. The ordinary and electron microscope are based upon the wave-like behaviour of light and electron respectively.

A localized particle's position in space can be accurately defined whereas a wave is spread out in space. Is it possible to define the position of electron in space? If it behaves like a particle, we should be able to locate it precisely. But if it behaves like wave, we cannot do so. A German physicist, Werner Heisenberg, tried in various ways to find the position of an orbiting electron but all in vain. He concluded in 1927 that there are definite limitations on the accuracy with which one can define the position of an electron. He showed that,

'There is an uncertainty Δx in the position and an uncertainty Δp in the momentum of subatomic object like an electron.'

This statement is known as uncertainty principle.

Heisenberg showed that the lower limit of this uncertainty is Planck's constant divided by 4π . Thus,

$$(\Delta p_x \Delta x \geq \frac{h}{4\pi})$$

Here Δp_x is the uncertainty in the momentum in the x direction and Δx is the uncertainty in the position. The sign \geq means the term $\Delta p_x \Delta x$ can be either greater than or equal to but never smaller than $\frac{h}{4\pi}$. If Δp_x is decreased Δx increases and vice-versa.

According to this principle, the more accurately one of these variables is specified, the more uncertain is the other. For instance, if velocity (or momentum) of a particle is determined with great accuracy, its

position becomes correspondingly less precise. Similarly, if the position is determined precisely, the momentum of the particle is not known with certainty. Thus, it is not possible to determine simultaneously the position and the momentum of small particles in motion accurately.

Exercise 4.7 Calculate the wavelength of an electron moving $3.0 \times 10^{10} \text{ cm s}^{-1}$ and of a baseball of 100 g moving at $3.0 \times 10^3 \text{ cm s}^{-1}$

Solution: The mass of an electron is $= 9.1 \times 10^{-31} \text{ kg}$; h is $6.6 \times 10^{-34} \text{ Js or kg m}^2 \text{ s}^{-1}$; v is $3 \times 10^{10} \text{ cm s}^{-1}$ or $3 \times 10^8 \text{ m s}^{-1}$. Thus, substituting the value of m , h and v in the relation $\lambda = h/mv$

$$\lambda = \frac{6.6 \times 10^{-34}}{9.1 \times 10^{-31} \times 3 \times 10^8} \frac{\text{kg m}^2 \text{ s}^{-1}}{\text{kg} \times \text{m s}^{-1}} = 2.4 \times 10^{-2} \text{ m}$$

The mass of a baseball is 100g or 0.1 kg v is $3 \times 10^3 \text{ cm s}^{-1}$ or $3 \times 10 \text{ ms}^{-1}$

Substituting for m , h and v :

$$\frac{6.6 \times 10^{-34}}{0.1 \times 3 \times 10} \frac{\text{kg m}^2 \text{ s}^{-1}}{\text{kg} \times \text{ms}^{-1}} = 2.2 \times 10^{-34} \text{ m}$$

Thus, from the wavelengths of an electron and a baseball, it is evident that small particles like electron follow de Broglie hypothesis and massive bodies like a baseball do not follow.

Exercise 4.8 What is the product of uncertainty in position and velocity for an electron of mass $9.11 \times 10^{-28} \text{ g}$ according to Heisenberg's uncertainty principle?

Solution: From Heisenberg's uncertainty principle.

$$\Delta x, \Delta p_x = \frac{h}{4\pi}$$

$$\text{or } \Delta x \cdot m \cdot \Delta v = \frac{h}{4\pi}$$

$$\Delta x \cdot \Delta v = \frac{h}{m 4\pi}$$

Substituting the value of m of an electron, we obtain,

$$\Delta x \cdot \Delta v = \frac{6.6 \times 10^{-34}}{4 \times 22 \times 9.1 \times 10^{-31}} \frac{\text{kg m}^2 \text{ s}^{-1}}{\text{kg}} = 57 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$$

In Bohr's model, the electron was supposed to move around the nucleus in any one of a limited number of circular orbits. Each orbit corresponds to an allowed energy level. Thus, in each orbit, the electron had a fixed and characteristic value of energy. A precise description of the position or the path of an electron, as suggested by Bohr's orbit, has been found impossible (uncertainty principle). A new theory that could describe the probable behaviour of electron in atoms and molecules has been developed. This theory is called **quantum mechanics**. The theory

cloud, which is densest at those points where the electron is most likely to be found and less dense where it is less likely to be found. A probability cloud is also often called an electron density cloud or an orbital.

Thus, the orbital of an electron is a part of space around the nucleus, where the electron stays most of its time and has a maximum probability of being traced.

The probability information, in turn, can be used to construct pictures (Fig. 4.34) of the region in space in which we are likely to find

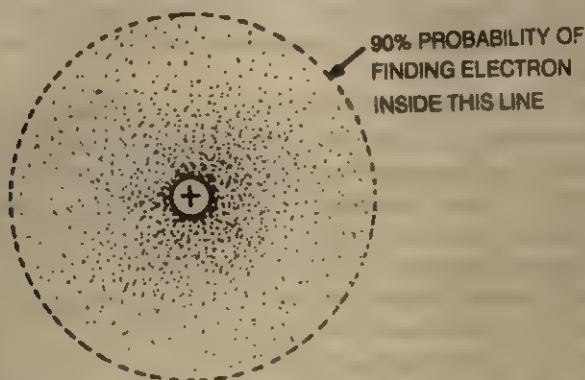


Fig. 4.34 Circular cross-section of spherical boundary surface enclosing 90-99% probability space for 1s orbital

the electron. The probability of finding an electron is greater near the nucleus and less away from the nucleus. In Fig. 4.34 a circular cross section of the boundary surface is superimposed over the electron density picture. Thus, the probability density representation for an electron is termed as electron orbital. Electron orbitals in atoms are called atomic orbitals.

In each orbital, the electron has a definite energy. The energy is lower if the electron density is pronounced near the nucleus. This is because the electron is strongly attracted when it is close to the nucleus. The change in energy from one orbital to another is not continuous but discontinuous, i.e., energy is quantized.

A number of orbitals are possible in a hydrogen atom. They are characterized by their size, shape and orientation. In turn, size, shape and orientation depend upon the concentration of electron density over a certain region and along certain directions.

4.4.9 Quantum Numbers

According to wave mechanics, the energy levels in the atom are composed of one or more orbitals. In atoms that have more than one electron, the distribution of the electrons about the nucleus is described

by the number and type of energy levels that are occupied. Therefore, to understand the arrangement of electrons in space it is necessary to examine the energy levels. This is best accomplished through a discussion of quantum numbers done below :

The first and perhaps the most important quantum number is called the **principal quantum number** which is symbolized by letter ' n '. It refers to the average distance of an electron from the nucleus. In a general way, it describes the effective volume of an electron orbital, i.e., size. The distance is related to the energy of the electron. ' n ' can have positive integral values 1,2,3, and so on referring to the first (or K), second (or L), third (or M), etc., main energy levels of the electrons in an atom.

The second quantum number is known as **angular momentum quantum number**. It is also known as **azimuthal, orbital, subsidiary or secondary quantum number**. It is designated by the letter ' l '. It determines the shape of the spatial region in which the electron is most probably found. It turns out that the numerical value for ' l ' can again be only integral number 0, 1,2,3,.....upto $n-1$.

Each principal energy level may be split into a number of sublevels (orbitals) according to the values of l . Thus when $n = 1$, $l = 0$ which means that the first level is not split. When $n = 2$, l can be 0 and 1 so that the second principal energy level is subdivided into two. In fact, the number of sublevels is equal to the value of n . Thus, l accounts for the appearance of the orbital.

To understand the distribution of electrons in the atom, each sub-level is described by a letter depending on the values of n and l . Any sub-level for which $l = 0$ is described by the letter ' s '. A sub-level with $l = 1$ is described by letter ' p '; sub-levels with $l = 2,3,4$, etc. are designated by letters ' d ' ' f ' ' g ', etc. respectively. The value of n is placed in front of each letter. Thus, $1s$ represents the energy level for which $n = 1$ and $l = 0$; $2p$ corresponds to $n = 2$, $l = 1$; $3d$ corresponds to $n = 3$, $l = 2$. This has been illustrated in Fig. 4.35. The letters chosen were derived from spectroscopic terms.

The third quantum number is known as the **magnetic quantum number**. Under the influence of the strong magnetic field some of the spectral lines, that appear as single lines in the absence of magnetic field, split into several lines (Fig. 4.36). The splitting suggests that energy levels are split when the atoms emitting radiations are placed in a magnetic field. The explanation of these lines lies in the introduction of magnetic quantum number. It has the symbol m_l because it controls the behaviour of l in a magnetic field.

It defines the orientation of a moving electron with the external magnetic field. The fact that spectral lines are split into a finite number

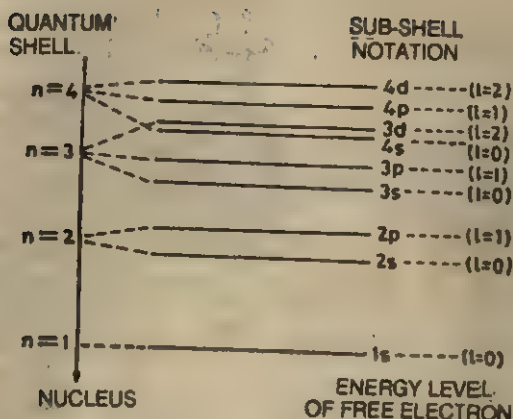


Fig. 4.35 Atomic energy levels

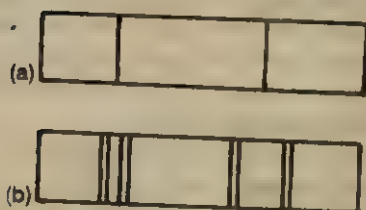


Fig. 4.36 Splitting of the D-lines in the sodium spectrum in a magnetic field (a) without magnetic field (b) with magnetic field.

of discrete line indicates that only a finite number of orientations are possible. These orientations are described by the Cartesian axes X, Y and Z.

The values that m_l can take are limited by the value of l . They are $-l, -(l-1), \dots, -1, 0, +1, \dots, +(l-1), +l$. Thus, if l is zero m_l can only take the value zero. If $l = 1$, m_l can be $-1, 0$ and $+1$. If $l = 2$, m_l can be $-2, -1, 0, +1, +2$. Since there are $2l + 1$ values of m_l for every given value of l , it follows that in the $2p$ level (or in fact any p-level) there are three values of m_l ($+1, 0$ and -1). Each value of m_l represents an atomic orbital. Thus, there will be three p orbitals for every value of n greater than 1. These p orbitals can be arranged in three different ways along the three co-ordinate axes, i.e., p_x, p_y and p_z . Similarly there is only a single s orbital for each value of n , (when $l = 0$) and five d orbitals ($d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}$ and d_{z^2}) for every value of $n = 3$ or more (when $l = 2$).

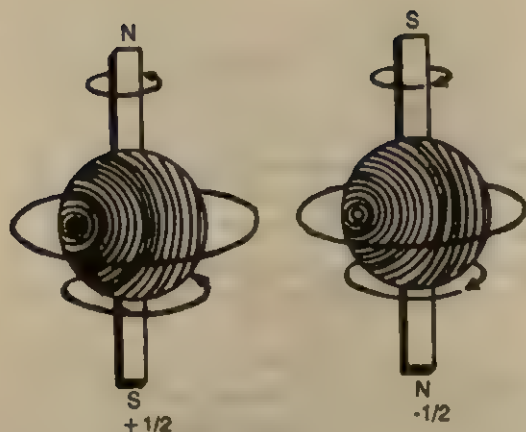


Fig. 4.37 Clockwise and anticlockwise spins of electrons around their own axes.

the phenomenon could not be interpreted in terms of the previous quantum numbers. It was proposed that these two lines originated from a moving electron spinning about its own axis. The spinning can be clockwise and anticlockwise (Fig. 4.37). Hence, this quantum number is called the **magnetic spin quantum number**.

The spin quantum number, designated by m_s , has a value of either $+ 1/2$ or $-1/2$ for any orbital of a specific n , l and m_l value. For example, for $n = 2$, $l = 0$, and 1 . There is one orbital (s) corresponding to the m_l value of zero for $l = 0$. There are three orbitals (the 2p orbitals) corresponding to the m_l values of $+ 1$, 0 , -1 for $l = 1$. For each of the orbitals, there is a $+ 1/2$ and a $- 1/2$ value of the m_s .

The four quantum numbers are listed below along with the values that may be assumed by each.

n = principal quantum number

= $1, 2, 3, \dots$

l = angular momentum quantum number

= $0, 1, 2, \dots, (n - 1)$

= m_l magnetic quantum number (for any value of n)

= $-, -(l-1), \dots, + (l-1), + l$

(for any value of l)

m_s = magnetic spin quantum number

= $+ 1/2, -1/2$

Every permitted combination of the three quantum numbers, n , l and m_l (a set of permitted values for the orbital) corresponds to a different electron orbital. All orbitals with same value of the principal quantum number, n are said to be in the same principal electronic shell or principal level and all orbitals with same value of l are in the same sub-shell or sub-level.

These three quantum numbers were found adequate to describe all the orbitals in atoms. To account for a doubling of certain single spectral lines (predicted by Bohr's theory), seen in the spectra of atoms with only one electron in the valence shell, "a fourth quantum number was introduced as

The principal shells are numbered according to the value of n . At times, they are also denoted by letters.

The energy of these orbitals for a specific shell say 4th shell, follows the sequence :

$$4s < 4p < 4d < 4f$$

The various orbitals have different energies and their arrangement according to increasing energy is shown in Fig. 4.38 and Fig. 4.39.

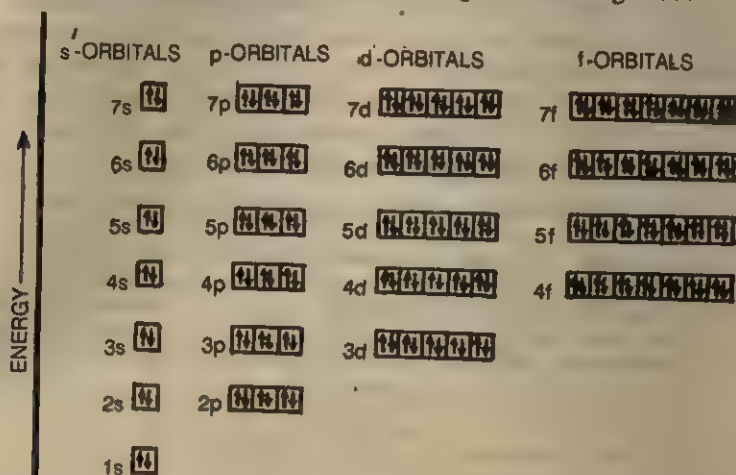


Fig. 4.38 Energy level diagram for hydrogen. The boxes depict orbitals. The various orbitals have different energies and are arranged in the increasing order of energy. In the case of hydrogen, energy levels are a function of principal quantum number. Hence, all the orbitals of the given principal shell of the hydrogen atom have the same energy. Orbitals with the same energies are said to be degenerate'.

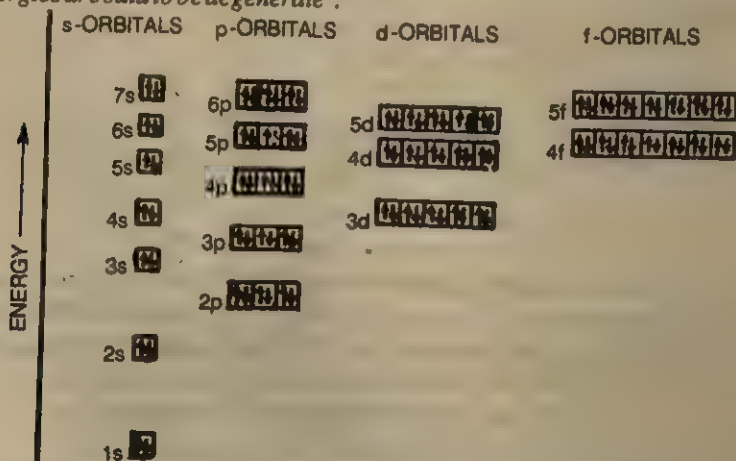


Fig. 4.39 Energy level diagram for atoms containing more than one electron.

4.4.10 Pauli's Exclusion Principle

This important principle was advanced by Wolfgang Pauli (1925) on the basis of experimental observations. It states that no two electrons in any atomic orbital can have all the four quantum numbers identical. Thus, two electrons in any atomic orbital with same values of n , l , and m_l must have two different values of the spin quantum number, m_s , i.e., either $+1/2$ or $-1/2$. In effect, this limits the number of electrons in any atomic orbital to two, and it also requires that the spins of these two electrons be in opposite directions, i.e., one has an 'up' spin clockwise and the other a 'down' spin anticlockwise. Thus, the maximum number of electrons that each s, p, d and f orbitals and different energy levels can have is given in Table 4.6.

Table 4.6 Distribution of electrons among the orbitals and quantum levels

Principal quantum number n	Angular momentum quantum number, l : values range from 0 to $n-1$	Magnetic quantum number m_l : values range from $+l$ to $-l$	Spin quantum number, m_s : Every one value of l has two values for m_s , i.e., $+1/2, -1/2$.	Designation of orbital	Maximum number of electrons in energy sublevel	Total number of electrons in main energy level
1 (K-shell)	0	0	$+1/2, -1/2$	1s	2	2
2 (L-shell)	0, 1	0, $+1, 0, -1$	$+1/2, -1/2$ $+1/2, -1/2$	2s 2p	2 6	8
3 (M-shell)	0, 1, 2	0, $+1, 0, -1$, $+2, +1, 0, -1, -2$	$+1/2, -1/2$ $+1/2, -1/2$ $+1/2, -1/2$	3s 3p 3d	2 6 10	18
4 (N-shell)	0, 1, 2, 3	0, $+1, 0, -1$, $+2, +1, 0, -1, -2$, $+3, +2, +1, 0, -1, -2, -3$	$+1/2, -1/2$ $+1/2, -1/2$ $+1/2, -1/2$ $+1/2, -1/2$	4s 4p 4d 4f	2 6 10 14	32

From the limitation on the permitted values of the quantum numbers, the number of orbitals in a shell of number n is given by n^2 . Since it is not possible to have more than two electrons in any one orbital, the maximum number of electrons in a shell must be $2n^2$ (Table 4.6), Figure 4.40 portrays permissible combinations of n , l and m_l and m_s .

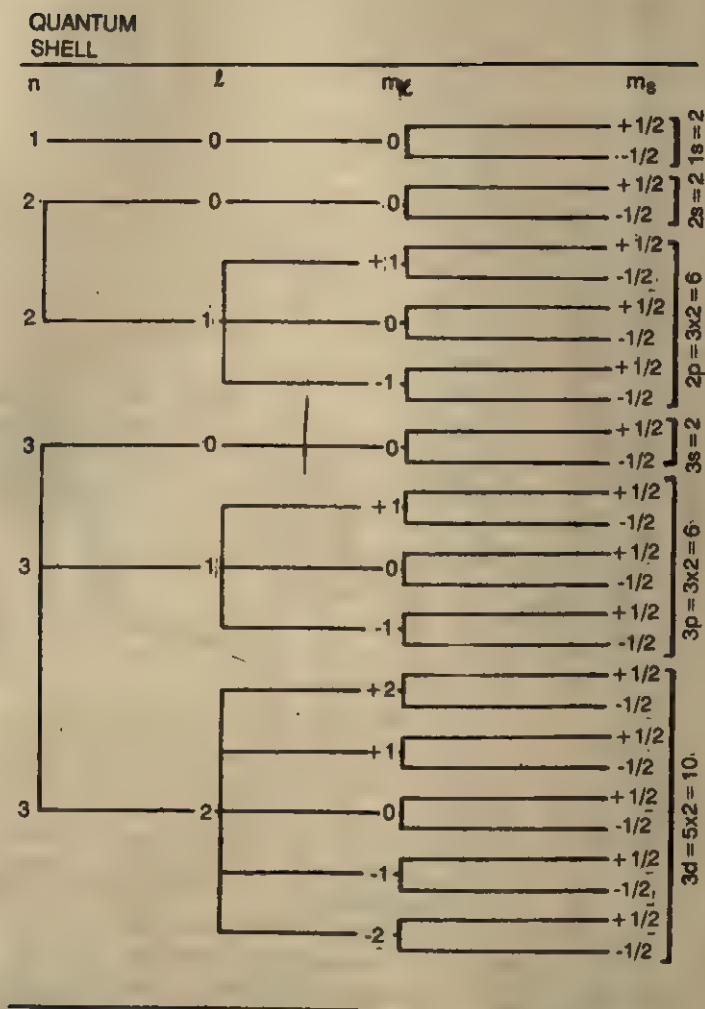


Fig. 4.40 Portraying of permissible combinations of n , l , m_l and m_s . The maximum number of electrons which s, p, d and f sub-shells can accommodate is also shown

Evidence for sub-shells (Orbitals) of Electrons and Distribution of Electrons Among the Orbitals

Figure 4.41 is a graph plotted between the first ionization energies of the elements against atomic numbers. To arrive at the information required, the graph can be divided into parts ending with a noble gas.

The graph between one noble gas and the next can also be divided

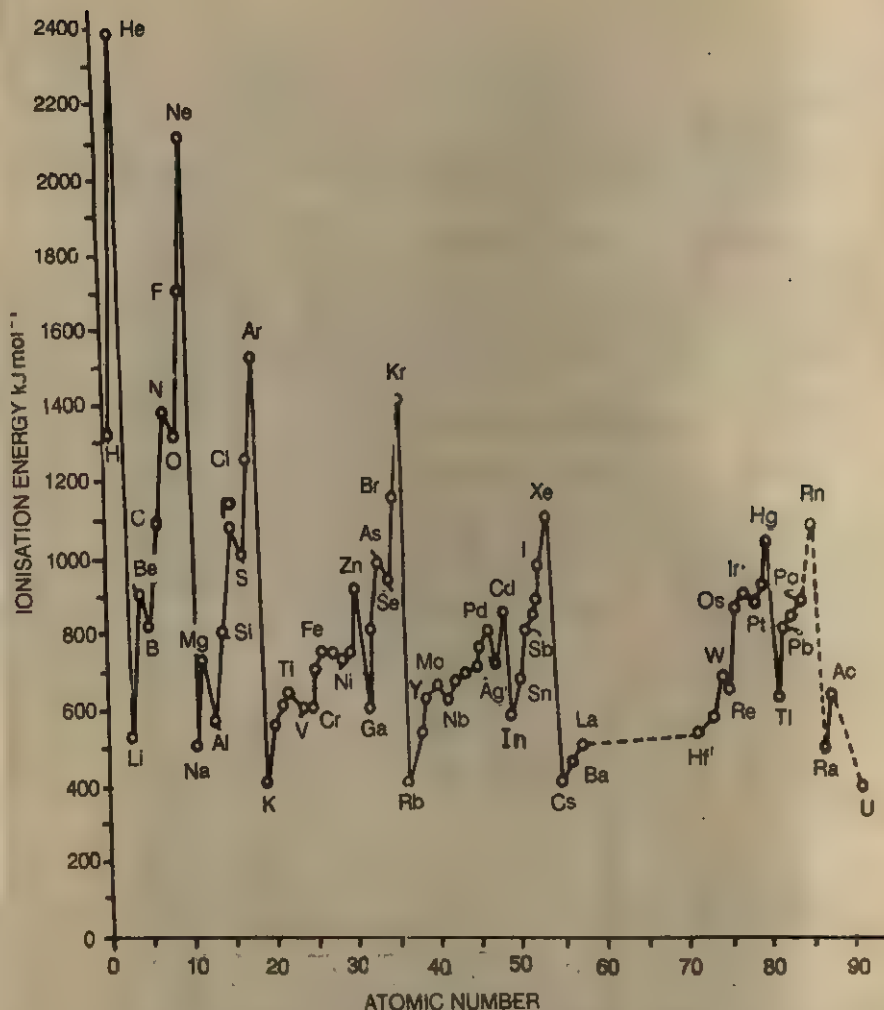


Fig. 4.41 First ionization energies of the elements

into sub-divisions. These sub-divisions contain either two, six, ten or fourteen points on the graph. For example, after He, Ne and Ar there are deep troughs in the graph followed by small intermediate peaks at Be; Mg and Ca, i.e., sub-divisions of two points. Immediately after Be and Mg there are groups of six points (B to Ne and Al to Ar). Between Sc and Zn there is a sub-division containing ten points.

In fact, the points on the graph in Fig. 4.41 between one noble gas and the next correspond to the filling of one shell with electrons. This means that the sub-divisions of points corresponds to sub-shells of electrons. Thus, the studies of both ionization energies and atomic spectra provide evidence for the presence of sub-shells (orbitals) among each quantum shell - and it also confirms the distributions of electrons among the orbitals as suggested through Table 4.6 and Fig. 4.40.

The electron structure of an atom can, therefore, be described in terms of its sub-levels (orbitals) occupied by electrons. A number (1,2,3, etc.) is used to denote the energy level (Figure 4.35), a letter (s, p, d or f) to denote the sub-level and superscript to indicate the number of electrons in the sub-level.

Thus, potassium has 2 electrons in the 1s sub-level (i.e., $1s^2$)
 2 electrons in the 2s sub-level (i.e., $2s^2$)
 6 electrons in the 2p sub-level (i.e., $2p^6$)
 2 electrons in the 3s sub-level (i.e., $3s^2$)
 6 electrons in the 3p sub-level (i.e., $3p^6$)
 and 1 electron in the 4s sub-level (i.e., $4s^1$)

The graph (Fig. 4.41) also shows that the electrons always occupy the lowest available energy sub-levels and that electrons 'pair-up' as soon as each sub-level is half-filled.

4.4.11 Shapes of Orbitals

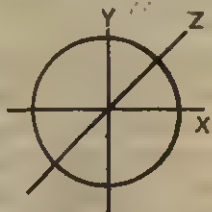
The orbitals are directly related to the probability of finding an electron in space around the nucleus. Generally, they are portrayed in the three dimensions using the Cartesian coordinate system (X, Y, Z axes) as a 'frame of reference. It is seen that the various types of orbitals have characteristic shapes.

The shape of an orbital depends on the value of the quantum number l . For an s orbital ($l = 0$) the shape is sphere, showing that all directions are equally likely to be inhabited by the electrons. The size of the orbital depends on the value of the principal quantum, n .

The electron cloud [Fig. 4.42 (a)] illustrates the probability of finding an electron in 1s orbital at certain positions near the nucleus. The density of dots is proportional to the probability of finding the electron at a specific point. Thus, the electron density falls off smoothly and rapidly with increasing distance from the nucleus although it never reaches zero. It is not possible to draw a picture of the orbital that in-



(A) DENSITY DOT DIAGRAM



(B) BOUNDARY REPRESENTATION

cludes all these dots as the pattern of dots extends in all directions and to all distances from the nucleus, but it is possible to include the major share of the electron cloud within a boundary surface and it is customary to represent the orbital by a

Fig. 4.42 Electron probability diagrams for 1s: (a) density dot diagram, and (b) boundary representation

single boundary line [Fig. 4.42 (b)] enclosing about 90% of the electron density.

For every value of n , both l and m_l assume zero value. Hence, all s orbitals in other energy shells, such as $2s$, $3s$, $4s$, etc. are spherically symmetrical about the nucleus.

Probability distribution pattern for an electron in $2p$ orbital does not assume a spherical symmetry. From the limitation on the permitted values of quantum numbers, there can be three p orbitals (p_x , p_y and p_z). They acquire dumb-bell shape and are oriented along the three mutually perpendicular X , Y and Z axes (Fig. 4.43). They are equal in energy.

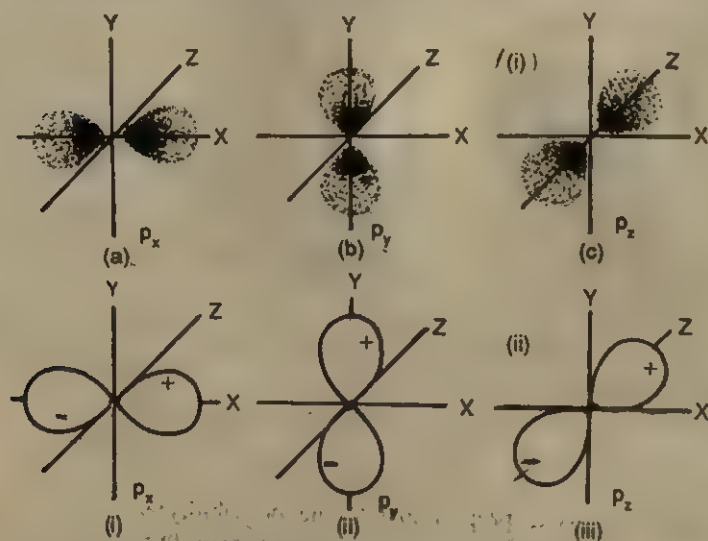


Fig. 4.43: Electron probability diagrams for p orbitals ; (a) (b) and (c) pattern of dots represent the relative probability of finding the electron and (i) (ii) and (iii) boundary representation of $2p$ orbitals.

The five $3d$ orbitals are shown in Fig. 4.44. Similar to p orbitals they also have directional characteristics. The basic shape of the d orbital is a four-lobed picture. The d_{z^2} orbital is not in conformity with the usual picture. The lobes are aligned along the Z -axis together with a tyre surrounding the Z -axis. The $d_{x^2-y^2}$ orbital is similar to d_{xy} orbital but rotated through 45° (energy for $d_{x^2-y^2}$ and d_{z^2} is same but different for d_{xy} , d_{yz} and d_{zx}). This is directed along X and Y axes. The three d_{xy} , d_{yz} and d_{zx} orbitals are alike and only differ in the plane which contains the axes. These planes are oriented to make angles of 45° with axes X , Y and Z .

Difference between $1s$ and $2s$

Figure 4.45 illustrates the pattern of electron density distribution

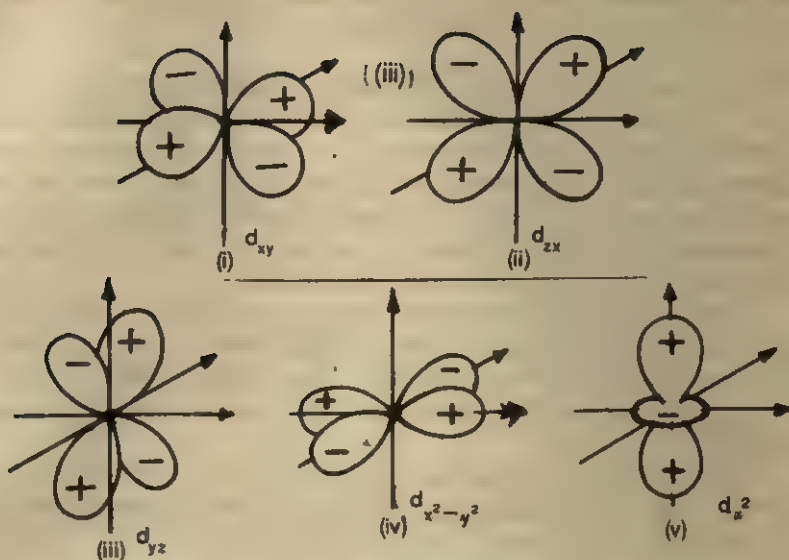
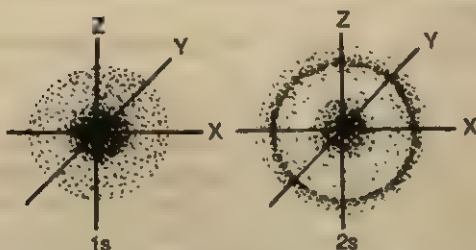


Fig. 4.44. Boundary representation of the shapes of five d orbitals.



in 1s and 2s orbitals. The probability of finding the electron in 1s orbital decreases as the distance from the nucleus increases.

From Fig. 4.45 it is evident that in 2s orbital there are two spherical regions - one closer to the nucleus and the other further away from the nucleus. Both these regions depict the probable electron density distribution. Thus, the important difference between 1s and 2s orbitals is that 2s is effectively larger (higher energy s orbitals having large radii). There is another significant feature of the 2s electron cloud that there exists a spherical region at an intermediate distance (undotted) where the probability of finding an electron is zero. This is called a nodal surface.

Difference between $2p_x$ and $2p_y$ and $2p_z$

All the three dumb-bell shaped $2p$ orbitals have directional properties. Two lobes acquire different algebraic signs i.e., +ve and -ve. [Fig. 4.43 (i), (ii), (iii)]. The three equivalent $2p$ orbitals differ only in their spatial orientations. The orbitals have regions of high probable electron

density along each axis. Each has one plane of zero electron density (eg., YZ plane in $2p_x$). It is called a nodal plane.

4.4.12 Electron Configuration of atoms (Aufbau Principle)

A designation which characterizes each electron in an atom is referred to as the electron configuration. The electron configuration of an element depicts the location and energy of the electrons. You are already familiar with the rules of writing the electron configurations of atoms. After learning about orbitals, it becomes appropriate to reconsider the topic and understand some additional features.

An atom in its lowest energy state is said to be in the ground state, stable or normal state. When an atom contains several electrons, they are assigned to orbitals according to the following rules, which are known collectively as the 'Aufbau principle' (aufbau in German means build up)

(i) In building up atomic structure, electrons seek to enter the orbital of the lowest energy. According to a definite pattern of orbitals the order is $1s, 2s, 2p, 3s, 3p, 4s, 3d$, etc. (Figs. 4.46 and 4.47).

(ii) A single orbital cannot have more than two electrons. When two electrons occupy the same orbital they must be of opposite spin (Pauli's exclusion principle).

(iii) In a set of degenerate orbitals (orbitals of the same energy)

the electrons occupy each orbital singly with the same spin before any pairing occurs (Hund's rule of maximum multiplicity).

There is another simple mnemonic device for electron configuration. This device suggests the use of six inverted similar triangles as shown in Fig. 4.47. On the left side, s orbitals are portrayed and the right side is used for p orbitals. The middle two bases are devoted to d orbitals and the upper most two bases to d and f orbitals. The triangle

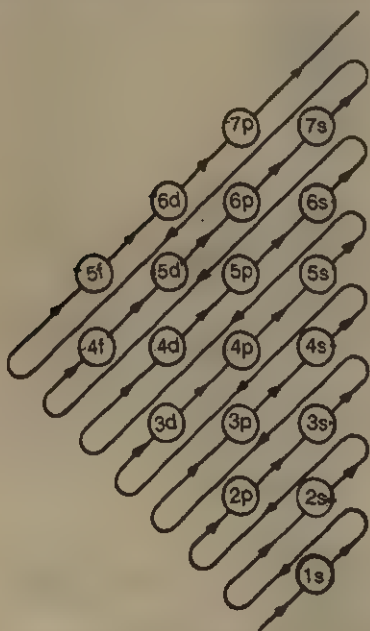


Fig. 4.46 Sequence for filling the orbitals

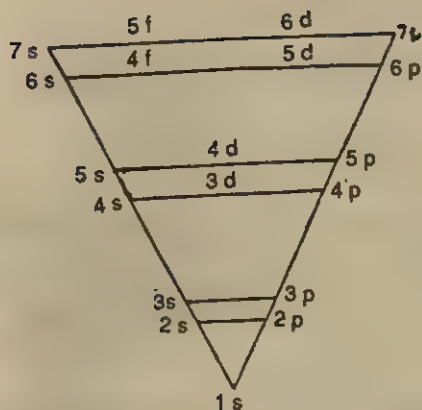


Fig. 4.47 Another simple way for filling orbitals

I. Sodium ($Z = 11$) $1s^2, 2s^2, 2p^6, 3s^1$

II. Sodium ($Z = 11$)

↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑
----	----	----	----	----	----	---

Method I depicts the total number of electrons in each orbital. Method II gives the break up of each orbital with the help of arrows (orientation of electron spin), upward arrow (↑) corresponds to $m_s = +1/2$, (clockwise) and downward arrow (↓) corresponds to $m_s = -1/2$, (anti-clockwise). Method II is not common for giving the electron configuration. It depicts certain features of the atom and its electronic configuration. Some examples given below explain the Hund's rule explicitly. For example,

Boron ($Z = 5$)

↑↓	↑↓	↑	.	.
----	----	---	---	---

Carbon ($Z = 6$)

↑↓	↑↓	↑	↑	.
----	----	---	---	---

The 6th electron goes into a new 2p orbital.

Nitrogen ($Z = 7$)

↑↓	↑↓	↑	↑	↑
----	----	---	---	---

The 7th electron also goes into a new 2p orbital. Thus, in nitrogen all the three 2p electrons are with parallel spins.

Oxygen ($Z = 8$)

↑↓	↑↓	↑↓	↑	↑
----	----	----	---	---

is read, from bottom to top and from left to right. Starting at the vertex labelled 1s; you follow the left side to the point labelled 2s and read across the base line to the point labelled 2p on the right side. This procedure is followed until all the electrons have been used.

Keeping in view the above given rules, two methods are adopted to designate electron configurations. For example sodium is represented,

The 8th electron must go into an orbital already occupied with an electron.

Flourine ($Z=9$):

↑↓

↑↓

↑↓	↑↓	↑
----	----	---

The 9th electron goes into one of the two orbitals containing single electron with parallel spins.

Neon ($Z = 10$):

↑↓

↑↓

↑↓	↑↓	↑↓
----	----	----

With the 10th electron in the neon atom all the orbitals are fully occupied, and thus, the second principal energy level is filled.

The electronic configuration of potassium explains that in arriving at electronic configuration the orbital with lower energy is always preferred over the orbital with higher energy.

Potassium ($Z= 19$); $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$

The 19th electron for potassium, K enters the 4s orbital instead of 3d. This means that 4s orbital is at lower energy level than 3d. Similarly we can have for calcium, *i.e.*,

Calcium ($Z = 20$); $1s^2 2s^2, 2p^6, 3s^2, 4s^2$

Since the first 18 electrons represent the configuration of argon, the configuration of calcium can be written as, Ca ; (Ar) $4s^2$

Now the 21st electron will populate the 3d orbital. Thus,

Scandium ($Z=21$); (Ar) $3d^1 4s^2$

Similarly zinc ($Z=30$); (Ar) $3d^{10} 4s^2$

Stability of Filled and Half-Filled Orbitals

Another factor that affects the ground state electronic configuration of certain atoms is the tendency for orbitals to become completely filled and exactly half-filled. For example, for chromium, Cr the electronic configuration is

Cr ($Z = 24$); (Ar) $3d^5 4s^1$

Instead of Cr ($Z = 24$); (Ar) $3d^4 4s^2$

This unexpected result occurs because a half-filled sub-shell possesses an extra added stability (*i.e.*, possesses lower energy).

Some other examples of this kind of deviation are :

Cu ($Z = 29$); Ar $3d^{10} 4s^1$

Mo ($Z = 42$); (Kr) $4d^5 5s^1$

In the case of copper, Cu the completely filled sub-level possesses extra stability. Another example of this kind of deviation using 5d and 4f levels is given below :

Gd ($Z = 64$); (Xe) $4f^8 6s^2$

(Expected configuration)

Gd ($Z = 64$) (Xe) $4f^7 5d^1 6s^2$

(Actual configuration)

Thus, in the case of Cr, Cu and Mo, the unexpected results are explained on the basis of the added stability of a completely filled or half-filled subshell. This concept of extra stability for half-filled and completely filled orbitals, is also seen in cases where the aufbau principle is followed. For example, N, P and As show unusual properties (e.g., unusual high ionization potentials) because they all have half-filled subshells. Similarly, Zn, Cd and Hg show some unusual properties because they all possess completely filled subshells. Thus, the p^3 , p^6 , d^5 , d^{10} , f^7 and f^{14} configuration, which are either filled or half-filled, are more stable.

In case of Gd and similar other cases (elements with higher atomic numbers), the variations are not because of the enhanced stability of filled or half-filled subshells.

In conformity with the above rules and discussion, electron configurations of the elements are given in Table 4.7.

TABLE 4.7. Electron configuration of the elements

Atomic number	Element	Electron configuration
1	H	_____ $1s^1$
2	He	_____ $1s^2$
3	Li	_____ $[He] 2s^1$
4	Be	_____ $2s^2$
5	B	_____ $2s^2 2p^1$
6	C	_____ $2s^2 2p^2$
7	N	_____ $2s^2 2p^3$
8	O	_____ $2s^2 2p^4$
9	F	_____ $2s^2 2p^5$
10	Ne	_____ $1s^2 2s^2 2p^6$
11	Na	_____ $[Ne] 3s^1$
12	Mg	_____ $3s^2$
13	Al	_____ $3s^2 3p^1$
14	Si	_____ $3s^2 3p^2$
15	P	_____ $3s^2 3p^3$
16	S	_____ $3s^2 3p^4$
17	Cl	_____ $3s^2 3p^5$
18	Ar	_____ $1s^2 2s^2 2p^6 3s^2 3p^6$
19	K	_____ $[Ar] 4s^1$
20	Ca	_____ $4s^2$
21	Sc	_____ $3d^1 4s^2$
22	Ti	_____ $3d^2 4s^2$
23	V	_____ $3d^3 4s^2$
24	Cr	_____ $3d^5 4s^1$

TABLE 4.7 Contd.

Atomic number	Element	Electron configuration
25	Mn	$3d^5 4s^2$
26	Fe	$3d^6 4s^2$
27	Co	$3d^7 4s^2$
28	Ni	$3d^8 4s^2$
29	Cu	$3d^{10} 4s^1$
30	Zn	$3d^{10} 4s^2$
31	Ga	$3d^{10} 4s^2 4p^1$
32	Ge	$3d^{10} 4s^2 4p^2$
33	As	$3d^{10} 4s^2 4p^3$
34	Se	$3d^{10} 4s^2 4p^4$
35	Br	$3d^{10} 4s^2 4p^5$
36	Kr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
37	Rb	$[Kr] 5s^1$
38	Sr	$5s^2$
39	Y	$4d^1 5s^2$
40	Zr	$4d^2 5s^2$
41	Nb	$4d^4 5s^1$
42	Mo	$4d^5 5s^1$
43	Tc	$4d^5 5s^2$
44	Ru	$4d^7 5s^1$
45	Rh	$4d^8 5s^1$
46	Pd	$4d^{10}$
47	Ag	$4d^{10} 5s^1$
48	Cd	$4d^{10} 5s^2$
49	In	$4d^{10} 5s^2 5p^1$
50	Sn	$4d^{10} 5s^2 5p^2$
51	Sb	$4d^{10} 5s^2 5p^3$
52	Te	$4d^{10} 5s^2 5p^4$
53	I	$4d^{10} 5s^2 5p^5$
54	Xe	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
55	Cs	$[Xe] 6s^1$
56	Ba	$6s^2$
57	La	$5d^1 6s^2$
58	Ce	$4f^1 6s^2$
59	Pr	$4f^2 6s^2$
60	Nd	$4f^4 6s^2$
61	Pm	$4f^5 6s^2$
62	Sm	$4f^6 6s^2$
63	Eu	$4f^7 6s^2$
64	Gd	$4f^7 5d^1 6s^2$
65	Tb	$4f^9 6s^2$

Contd.

TABLE 4.7 Contd.

Atomic number	Element	Electron configuration
66	Dy	$4f^{10}6s^2$
67	Ho	$4f^{11}6s^2$
68	Er	$4f^{12}6s^2$
69	Tm	$4f^{13}6s^2$
70	Yb	$4f^{14}6s^2$
71	Lu	$4f^{14}5d^1 6s^2$
72	Hf	$4f^{14}5d^2 6s^2$
73	Ta	$4f^{14}5d^3 6s^2$
74	W	$4f^{14}5d^4 6s^2$
75	Re	$4f^{14}5d^5 6s^2$
76	Os	$4f^{14}5d^6 6s^2$
77	Ir	$4f^{14}5d^7 6s^2$
78	Pt	$4f^{14}5d^9 6s^1$
79	Au	$4f^{14}5d^{10} 6s^1$
80	Hg	$4f^{14}5d^{10} 6s^2$
81	Tl	$4f^{14}5d^{10} 6s^2 6p^1$
82	Pb	$4f^{14}5d^{10} 6s^2 6p^2$
83	Bi	$4f^{14}5d^{10} 6s^2 6p^3$
84	Po	$4f^{14}5d^{10} 6s^2 6p^4$
85	At	$4f^{14}5d^{10} 6s^2 6p^5$
86	Rn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$
87	Fr	$[Rn] 7s^1$
88	Ra	$7s^2$
89	Ac	$6d^1 7s^2$
90	Th	$6d^2 7s^2$
91	Pa	$5f^2 6d^1 7s^2$
92	U	$5f^3 6d^1 7s^2$
93	Np	$5f^4 6d^1 7s^2$
94	Pu	$5f^6 7s^2$
95	Am	$5f^7 7s^2$
96	Cm	$5f^7 6d^1 7s^2$
97	Bk	$5f^9 6d^1 7s^2$
98	Cf	$5f^{10} 7s^2$
99	Es	$5f^{11} 7s^2$
100	Fm	$5f^{12} 7s^2$
101	Md	$5f^{13} 7s^2$
102	No	$5f^{14} 7s^2$
103	Lr	$5f^{14} 6d^1 7s^2$
104	(Ku)	$5f^{14} 6d^2 7s^2$
105	(Ha)	$5f^{14} 6d^3 7s^2$

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

- 4.1. Put a tick (✓) mark against the suitable choice:
- (i) Which one of the following descriptions of cathode rays is not correct ?
 - (a) Move in a straight line
 - (b) Depend upon the nature of the gas used in a discharge tube.
 - (c) Cast shadow of the solid object placed in their path.
 - (d) Are deflected towards the positive pole of the magnetic field.
 - (ii) Isotopes of an element have :
 - (a) same number of neutrons
 - (b) same atomic number
 - (c) same atomic mass
 - (d) same number of protons
 - (iii) Which of the following arrangements of electrons represent aluminium ?
 - (a) 2, 8, 1 (b) 2, 8, 2 (c) 2, 8, 3 (d) 2, 8, 4
 - (iv) Which of the following statements is not correct for Bohr's model of atom ?
 - (a) The nucleus of an atom is situated at its centre.
 - (b) The electrons move in circular orbits.
 - (c) Electrons can jump from one orbit to another.
 - (d) An electron neither loses nor gains energy in jumping from one orbit to another.
 - (v) Which of the following statements is not correct ?
 - (a) The whole mass of an atom is concentrated in the nucleus.
 - (b) Valence electrons are involved in chemical bond formation.
 - (c) Atomic number represents the number of protons contained in the nucleus.
 - (d) Both deuterium and tritium contain 2 protons each.
 - (vi) When alpha particles are sent through a thin metal foil, most of them go straight through the foil because (IIT 1984)
 - (a) alpha particles are much heavier than electrons.
 - (b) alpha particles are positively charged.
 - (c) most part of the atom is empty space.
 - (d) alpha particles move with high velocity.
 - (vii) The radiation from a naturally occurring radioactive substance as seen after deflection by a magnetic field in one direction are : (IIT 1984)
 - (a) definitely alpha rays.
 - (b) definitely beta rays.
 - (c) both alpha and beta rays.
 - (d) either alpha or beta rays.
 - (viii) Correct set of four quantum numbers for the valence (outermost) electrons of rubidium ($Z=37$) is;
 - (a) $5, 0, 0, +1/2$ (b) $5, 1, 0, +1/2$ (c) $5, 1, 1, +1/2$ (d) $6, 0, 0, +1/2$
 - (ix) Which electron level would allow the hydrogen atom to absorb a photon but not to emit a photon ? (IIT 1984)
 - (a) $3s$ (b) $2p$ (c) $2s$ (d) $1s$
 - (x) The radius of an atomic nucleus is of the order of : (IIT 1985)
 - (a) 10^{-10} cm (b) 10^{-13} cm (c) 10^{-15} cm (d) 10^{-6} cm
 - (xi) Rutherford's alpha particle scattering experiment eventually led to the conclusion that: (IIT 1986)
 - (a) mass and energy are related.
 - (b) electrons occupy space around the nucleus.
 - (c) neutrons are buried deep in the nucleus.
 - (d) the point of impact with matter can be precisely determined.

- (xii) Which one of the following sets of quantum numbers represents as impossible arrangement ? (IIT 1986)

	n	l	m_l	m_s
(a)	3	2	-2	$1/2$
(b)	4	0	0	$1/2$
(c)	3	2	-3	$1/2$
(d)	5	3	0	$-1/2$

- (xiii) The wavelength of a spectral line for an electronic transition is inversely related to
 (a) the number of electrons undergoing the transition. (IIT 1988)
 (b) the nuclear charge of the atom.
 (c) the difference in the energy of the energy levels involved in the transition
 (d) the velocity of the electron undergoing the transition.

- (xiv) The outermost electronic configuration of the most electronegative element is : (IIT 1988)

(a) ns^2np^3 (b) ns^2np^4 (c) ns^2np^5 (d) ns^2np^6

- (xv) Which of the following atoms has the largest number of unpaired electrons in its ground state configuration ?

(a) Co (b) Mn (c) Zn (d) Ag

- (xvi) Of the quantum state designations given below which does not describe an allowed state for an electron in an atom ?

I	$n = 3, l = 2, m_l = -2$
II	$n = 3, l = 1, m_l = 0$
III	$n = 3, l = 0, m_l = -1$
IV	$n = 3, l = 2, m_l = 0$
V	$n = 3, l = 3, m_l = -2$

(a) 1 and 15 (b) 2 and 13 (c) 3 and 14 (d) 3 and 15

- 4.2 Match the descriptions in column B with the terms/statements in Column A.

Column 'A'	Column 'B'
1 Mass of an atom	(i) Determines the size of the orbital
2 Valence electrons	(ii) Copper
3 Isotopes	(iii) Concentrated in the nucleus
4 Electrons	(iv) Take part in chemical bonding
5 Atomic number	(v) Visible light
6 Mass number	(vi) Number of protons in the nucleus
7 $3d^{10} 4s^1$	(vii) Number of protons and neutrons in the nucleus
8 Principal quantum number	(viii) Nuclei that differ in their masses
9. Balmer series	(ix) Electromagnetic radiation
10. Light	(x) Extra nuclear region

- 4.3. Fill in the blanks in the followings:

- The maximum number of electrons in an energy level is given by the formula
- The andcharge of an atom are concentrated in its nucleus.
- Cathode rays consist ofcharged particles while canal rays arecharged.
- The neutral atomic particles, thewere discovered byand are located in theof the atoms.
- If a neutral atom contains 16 electrons, it will contain.....
- Bright line spectra arise when excitedexist.....energy in returning to their orbits.
- An orbital may accommodate.....electrons paired in opposite.....
- The first energy level has oneshaped.....orbitals.
- In building up atomic structureseek the lowest
- Theenergy level has five lobe shapedorbitals which can holdelectrons.

4.4 State if the following statements are True or False.

- (i) All atoms of a given element contain the same number of protons in their nuclei and electrons outside their nuclei.
- (ii) The addition of neutrons to the nucleus of an atom would increase the atomic number.
- (iii) The atomic number of an element accounts for the number of positive charges in the nucleus.
- (iv) Isotopes of an element differ in the number of neutrons.
- (v) Electrons move in definite energy levels.
- (vi) The atomic number of potassium is 23.
- (vii) Orbital quantum number describes the size of the orbital.
- (viii) An orbital can contain only two electrons.
- (ix) Lambda represents the frequency of electromagnetic radiations.
- (x) Electron microscope is based on the wave-like behaviour of electrons.

SHORT ANSWER QUESTIONS

4.5 Give answers to each in one or two words or a sentence.

- (i) What is the number of neutrons in an element whose mass number and atomic number are 18 and 7 respectively?
- (ii) If both K and L shells of an atom are full, what is the total number of electrons contained in them?
- (iii) What is Rutherford's atomic model?
- (iv) In what way cathode rays are different from canal rays?
- (v) What is nucleus?
- (vi) Does the atomic number of an element change when its atoms form ions?
- (vii) The atomic number of chlorine is 17. What is the number of electrons in Cl^- ions?
- (viii) An element has three electrons in the M shell. What is the atomic number of the element? Name the element.
- (ix) Two atomic species say A and B have 6 protons each. But A and B have 6 and 8 neutrons respectively. What is the relation between the two?
- (x) Why is the ratio e/m for positive rays different for different gases?

4.6 (i) An atomic orbital has $n = 3$, what are the possible values of l ?

(ii) An atomic orbital has $l = 2$ what are the possible values of m_l ?

(iii) Describe the orbital with the following quantum numbers:

(a) $n = 2, l = 0$

(b) $n = 4, l = 3$

(c) $n = 3, l = 1$

(iv) Give the electronic configurations for the ground state of the following atoms:

(a) N ($Z = 7$),

(b) Al ($Z = 13$),

(c) Cr ($Z = 24$),

(d) Rb ($Z = 37$)

(v) State which of the following sets of quantum numbers are possible. Give reasons for your answers.

1. $n = 0, l = 0, m_l = 0, m_s = +1/2$

2. $n = 1, l = 0, m_l = 0, m_s = -1/2$

3. $n = 1, l = 1, m_l = -1, m_s = +1/2$

4. $n = 1, l = 0, m_l = -1, m_s = +1/2$

5. $n = 2, l = 1, m_l = 0, m_s = +1/2$

6. $n = 2, l = 2, m_l = 0, m_s = +1/2$

7. $n = 2, l = 1, m_l = 0, m_s = -1/2$

(vi) What is light?

(vii) Define atomic orbital.

(viii) What do you understand by quantum numbers?

(ix) What is atomic spectrum?

(x) What is the special characteristic of p orbitals?

TERMINAL QUESTIONS

- 4.1 (a) How many electrons can there be in each orbital? How are two electrons in an orbital alike? How are they different?
(b) What happens when there are a number of orbitals of equal energy, such as the three 2p orbitals?
- 4.2 A neutral atom has electronic structure $1s^2 2s^2 2p^6 3s^2 3p^4$. Deduce as many of the following as you can from this information only :
(a) the atomic number of the element,
(b) the atomic mass of the element
(c) the number of electrons in the valence shell, and
(d) the number of unpaired electrons in the atom.
- 4.3 (a) Explain why chromium and copper have only one electron in their 4s sub-shell?
(b) Match each of the following quantum number values with the proper letter designation (K, L, M, N, s, p, d, f) :
(i) $n = 2$, (ii) $l = 3$, (iii) $l = 2$ (iv) $n = 3$, (v) $l = 0$
- 4.4 (a) Name the elements that have the following ground state electronic configurations in their outershell or shells.
1 $3s^2, 3p^6, 3d^7, 4s^2$
2 $4s^2, 4p^3$
3 $4s^2, 4p^6, 4d^{10}, 5s^1$
4 $5s^2, 5p^6, 6s^1$
5 $5s^2, 4p^4$
(b) Give the ground state electronic configuration for the following ions :
 Ca_{20}^{2+} , Cu_{29}^{+} , Ag_{47}^{+} , Cl_{17}^{-} , Co_{27}^{3+}
Also state the number of unpaired electrons in each of the ions listed above.
- 4.5 (a) What are the possible values of l , m_l , and m_s for an electron located in the 4th principal shell?
(b) Is the aufbau process of filling of energy sub-levels always followed?
- 4.6 For each of the following parts describe how many sets of quantum numbers are possible so that each set contains all the values listed?
(a) $n = 5, l = 4$, (b) $n = 4, l = 1$, (c) $n = 4, l = 0, m_l = 0$, (d) $n = 2, l = 0, m_s = +2$,
(e) $n = 3, l = 2, m_l = +1$ (f) $n = 2, l = 2$, and (g) $n = 5$.
- 4.7 (a) List all the values of n , l and m_l and m_s for each of the last electron of the following:
 F_9 , Mg_{12} , Al_{13} , Fe_{26} , Kr_{36} , and Cs_{55}
(b) Name the lowest shell which has a f sub-shell.
(c) How many electrons can be placed in an atomic orbital for which $l = 4$?
(d) Give the various possible values of m_l for an electron with $l = 2$.
(e) Give the various possible values of l for an electron with $n = 4$.
- 4.9 Discuss electrons, protons and neutrons with respect to location, mass and charge.
- 4.10 Discuss the contributions of Rutherford to the structure of the atom.
- 4.11 What is the basis of Bohr's model of atom? How did it account for the shortcomings of Rutherford's model of atom?
- 4.12 State the essential features of Bohr's atomic theory. What are its drawbacks?
- 4.13 What do you understand by quantum numbers? What is their significance regarding the energy, shape and orientation of electron orbitals?

- 4.14 State Pauli's exclusion principle. How does it affect the arrangement of electrons in an atom ?
- 4.15 Define the followings
 (i) Heisenberg's uncertainty principle
 (ii) Aufbau principle
 (iii) Orbital
 (iv) Energy level
- 4.16 Describe the distribution of electrons among the various energy levels in the terms of quantum numbers.
- 4.17 State the rules governing the filling of various orbitals with electrons.
- 4.18 Give the electronic configuration of nitrogen and copper.
 Explain their extra stability.
- 4.19 (a) Describe the shapes of s and p orbitals.
 (b) In what ways do the spatial distributions of the orbitals in each pair differ from each other ?
 (i) 1s and 2s, (ii) 2s and 2p_x, and (iii) 2p_y and 2p_z
- 4.20 In what ways is the wave mechanical model of atom an improvement over particle model ?
 (Hint); The wave equation only accounts for the relative probability of the electron being at a certain position with respect to the nucleus. In this respect it is in agreement with the uncertainty principle. The particle model (Bohr's model) is based upon the concept of exact positions for electron.
- 4.21 Draw probable electron density diagrams for various orbitals. What do these shapes of orbitals signify ?
- 4.22 Give the energy level diagram for the various orbitals of hydrogen. How does it differ from the energy level diagram for atoms other than hydrogen ?
- 4.23 Describe the photoelectric effect. How does it help in understanding the dual nature of matter and radiation ?
- 4.24 How many electrons can be placed in each main energy level ? Explain the arrangement in terms of quantum numbers.

ANSWERS TO SELF ASSESSMENT QUESTIONS

- 4.1 (i) b, (ii) b, (iii) c, (iv) d, (v) d, (vi) a and c, (vii) d, (viii) a, (ix) d, (x) b, (xi) b, (xii) c, (xiii) c, (xiv) c (xv) a (xvi) d.
- 4.2 1. (iii), 2. (iv), (3) (vii), (4) (x), 5 (vi), 6. (vii), 7. (ii), 8. (i) 9. (v) 10. (ix).
- 4.3 (1) $2n^2$ (2) mass, positive, (3) negatively, positively
 (4) neutrons, Chadwick, nucleus (5) sixteen protons,
 (6) electrons, electromagnetic, (7) two, spin (8) spherical, s (9) electrons, energy level,
 (10) third, d, ten.
- 4.4 (1) True, (2) False, (3) True, (4) True, (5) True, (6) False (7) False, (8) True, (9) False, (10) True.
- 4.5 (i) 11 neutrons
 (ii) 10 electrons

- (iii) It consists of a positive nucleus around which electrons are revolving.
- (iv) Cathode rays are composed of negatively charged particles (electrons) while canal rays are composed of positively charged ions.
- (v) The small positively charged central part of an atom is called nucleus.
- (vi) Atomic number of an element does not change when it forms ions because the number of protons remains the same.
- (vii) 18 electrons
- (viii) 13, Aluminium
- (ix) Isotopes of carbon $^{12}_6\text{C}$, $^{14}_6\text{C}$
- (x) Positive rays are produced by the loss of electrons from gaseous atoms, and hence, different gases would produce positive rays of different masses, and thus, of different e/m values.

4.6

- (i) $l = 0, 1, 2$
- (ii) $m_l = -2, -1, 0, +1, +2$
- (iii) (a) 2s, (b) 4f, (c) 3p
- (iv) (a) $1s^2, 2s^2, 2p^3$
 (b) $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$
 (c) $1s^2, 2s^2, 2p^6, 3s^2, 3d^5, 4s^1$
 (d) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 5s^1$
- (v)
 1. Not possible as n never assumes zero value
 2. Possible as for $n = 1$, the values for other quantum numbers are permissible.
 3. Not possible as l cannot be 1 when $n = 1$
 4. Not possible, as m_l cannot be -1 when $l = 0$
 5. Possible, as for $n = 2$ the values for other l quantum numbers are permissible.
 6. Not permissible, as cannot be 2 when $n = 2$
 7. Possible as for $n = 2$, the values for other quantum numbers are permissible.
- (vi) Light is a form of energy. Light may be described as electromagnetic radiations because they have waves which possess both electrical and magnetic properties.
- (vii) The region in space around the nucleus in which there is high probability of locating the electron.
- (viii) Quantum numbers are the set of four integers necessary to specify the energy (size), shape, orientation of the orbital to which an electron belongs.
- (ix) It is composed of lines which are spaced over the entire range of wavelengths of radiation emitted by the atoms of an element.
- (x) They have got directional property.

Chemical Families-Periodic Properties

————— If you have had your attention directed to the novelties in thought in your own lifetime, you will have observed that almost all really new ideas have a certain aspect of foolishness when they are first produced.

ALFRED NORTH WHITEHEAD
(1861-1947)

UNIT PREVIEW

- 5.1 Introduction
- 5.2 Early attempts for classification of elements
- 5.3 Mendeleev's periodic table
- 5.4 Modern basis of classification
- 5.5 The modern periodic table—the long form
- 5.6 Types of elements
 - 5.6.1 Noble gases
 - 5.6.2 Representative elements (s and p-block)
 - 5.6.3 Transition elements (d-block elements)
 - 5.6.4 Inner-transition elements
- 5.7 Periodic properties—the periodic table. Periodic trends in properties of elements
 - 5.7.1 Valence
 - 5.7.2 Atomic radius (size) of atoms and ions
 - 5.7.3 Density, melting point and boiling point
 - 5.7.4 Ionization energy
 - 5.7.5 Electron affinity
 - 5.7.6 Metallic and non-metallic nature of the elements
 - 5.7.7 Properties of hydroxides of alkali metals
 - 5.7.8 Properties of halides of alkali and alkaline earth metals
 - 5.7.9 Properties of sulphates and carbonates of alkali and alkaline earth metals
- Self assessment questions
- Terminal questions
- Answers to self assessment questions

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Emphasize the need of classifying elements.
2. Describe the early attempts to classify the elements.
3. Explain what is meant by the term periodicity as applied to the elements.
4. Describe the criterion of classifying elements adopted by Mendeleev.
5. State the periodic law and understand its significance.
6. Sketch the arrangement of groups and periods on the periodic table.
7. Illustrate the position of related groups of elements on the periodic table.
8. Put forward the modern basis of classifying elements.
9. Give the merits and demerits of the long form of periodic table.
10. Describe the variation in metallic nature, valence, atomic radius, density, melting and boiling points, ionization energy, electron affinity and properties of halides, hydroxides, sulphates and carbonates of alkali and alkaline earth metals.

5.1 INTRODUCTION

Today 107 elements are known and with the steady development of new ways of synthesizing elements this number is bound to continue increasing. Their systematic study would present quite a formidable problem but for the fortunate fact that they could be grouped together in sets or groups based on certain similarities and regularities in their properties.

During the 19th century, many elements were discovered along with detailed knowledge of their physical and chemical properties. The elements differed from one another in many of their properties. Some were soft and powdery, while others were hard and shiny ; some were gases and others were liquids at ordinary temperatures, and so on. It was also found that certain elements resembled with one another in some respects. The compounds formed by the combinations of elements revealed both some resemblances and differences among the elements. It was found that sodium and potassium metals have many similarities in their properties (Table 5.1).

TABLE 5.1

Property	Sodium, Na	Potassium, K
Valency in the compounds	Monovalent	Monovalent
Reaction with water	Reacts	Reacts
Nature of oxides	Na_2O (Basic)	K_2O (Basic)
Nature of hydroxides	NaOH , a strong alkali	KOH , a strong alkali
Nature of carbonates	Na_2CO_3 (alkaline), soluble in water	K_2CO_3 (alkaline) soluble in water

Similarly, alkaline earth metals, Ca, Sr, and Ba were found to show a marked resemblance. They show a valency of 2. Their oxides, hydroxides, carbonates, *etc.* show bivalency. Their oxides react with water to form hydroxides, $\text{M}(\text{OH})_2$. Their carbonates are soluble in water and on heating give same products, *i.e.*, $\text{MO} + \text{CO}_2$.

Fluorine, chlorine, bromine and iodine were found to show similarity in properties to a large extent. They are very reactive non-metals and exist in the combined state. Under normal conditions they exist as diatomic molecules in which the atoms are held together with covalent bonds. All halogens react with hydrogen under different conditions and form covalent hydrohalides which are soluble in water and produce aqueous solutions known as hydrofluoric, hydrochloric, hydrobromic and hydroiodic acids. They react with active metals like Na, Mg, *etc.*, forming halides which are electrovalent in nature. They exhibit univalency in all these compounds.

Nitrogen and phosphorus ; oxygen and sulphur; *etc.* were found to show a significant chemical resemblance. Both the nitrogen and phos-

phorus show trivalency (e.g., NH_3 , PH_3) and pentavalency (e.g., N_2O_5 , P_2O_5 or P_4O_{10}) in their compounds. Both the oxides (N_2O_5 and P_4O_{10}) are strongly acidic (HNO_3 and H_3PO_4). Their halides (NX_3 and PX_3) are covalent in nature.

Thus, certain similarities and regularities do exist among elemental substances, and these serve as the basis for a detailed and very useful classification of the elements. It was from attempts to relate the chemical and physical properties of the elements and their compounds to their atomic masses that the periodic table was born.

The formulation of the periodic table marked the beginning of a new era in chemistry. The periodic table presents a systematic and vital framework for organizing the facts and informations available on the chemical behaviour of both elements and compounds into a few simple and logical patterns. In this unit, we shall take up the facts that led to the development of Mendeleev's periodic table and see how this classification follows as a logical consequence of the arrangement of electrons in atoms. The body of this unit also includes the periodic trends in the physical and chemical properties of the elements.

5.2 EARLY ATTEMPTS FOR CLASSIFICATION OF ELEMENTS

Elements were, first of all, divided by Lavoisier into two groups (i) metals, and (ii) non-metals. Elements with metallic lustre, malleability, ductility, good conductivity of heat and electricity were identified as metals whereas the remaining elements were known as non-metals. This classification did not prove to be very useful as some elements, called metalloids, exhibited some properties characteristic of both metals and non-metals. It was also attempted to classify the elements on the basis of their acidic and basic character. This method also proved unsatisfactory as no clear distinction could be made. It varied according to experimental conditions.

Following the development of atomic theory and the determination of the atomic masses of a large number of elements with a reasonable accuracy, attempts were made to find a relationship between atomic mass which seemed to be fundamental and chemical properties.

In 1815, William Prout suggested that all the elements were formed by the simple aggregation of hydrogen atoms keeping in view that all atomic masses were whole number multiples of the atomic mass of hydrogen. However, soon it was found that most of the elements possessed fractional atomic masses. The hypothesis was, thus, not taken seriously. But no sooner had Prout's proposal been abandoned than the attempts of several other scientists to order and classify the elements appeared.

Dobereiner's Triads

In 1829, J.W. Dobereiner arranged closely related elements in groups of three, *i.e.*, triads, where the atomic masses of the middle elements were nearly the arithmetic mean of the other two. Some triads are listed in Table 5.2.

Little attention was paid to this observation at that time as some other groups of triads such as arsenic, antimony, bismuth and zinc, cadmium, mercury did not conform to the law.

TABLE 5.2 Dobereiner triads

		Triad		Mean atomic mass (amu)	
Element	Lithium	Sodium	Potassium	$\frac{7 + 39}{2}$	= 23
Atomic mass	7	23	39	2	
Element	Calcium	Strontium	Barium	$\frac{40 + 137.4}{2}$	= 88.7
Atomic mass	40	87.6	137.4	2	
Element	Chlorine	Bromine	Iodine	$\frac{35.5 + 127}{2}$	= 81.15
Atomic mass	35.5	80	127	2	
Element	Sulphur	Selenium	Tellurium	$\frac{32.2 + 129.2}{2}$	= 80.7
Atomic mass	32.2	79.3	129.2	2	

Newlands' Law of Octaves

The next attempt for classifying the elements was made by John Newlands (1864). He arranged elements according to increasing atomic masses. Starting with any given element, every element resembled in properties to the first, similar to the repetition of musical notes in, scales of eight. He called this generalization 'the law of octaves'. His scheme was somewhat as follows :

Li	Be	B	C	N	O	H
Na	Mg	Al	Si	P	S	F
K	Ca	Cr	Ti	Mn	Fe	Cl

The scheme failed on attempting to extend it beyond calcium. Elements beyond calcium appeared out of place in Newlands' scheme. This happened because many elements had not been discovered at that time and Newlands did not provide any blank space for them in his scheme. Newlands' rule did not hold true at all. Indeed his ideas met with ridicule from other scientists, one of whom suggested that it would be just as valuable to arrange the elements in alphabetical order. The importance of Newlands' contribution was finally acknowledged in 1887, when he was awarded the Davy Medal by the Royal Society.

Mendeleev and others developed further the idea of Newlands. Newlands deserves credit for recognizing the periodic recurrence of properties based on increasing atomic mass—an idea that formed the basis for later classifications of the elements.

5.3 MENDELEEV'S PERIODIC TABLE

The Periodic Law : Dimitri Ivanovitci Mendeleev - a Russian and Jullius Lothar Meyer - a German, working independently developed a classification scheme of the elements known at that time. Almost simultaneously, in 1869, these men published their versions of the classification. Meyer's work was based mainly on physical properties such as atomic volume, fusibility and brittleness. Mendeleev developed his ideas about the periodicity of the elements by comparing the chemical properties of the elements and their compounds. Their classifications were based upon the periodic law, which states that "if the elements are arranged in order of increasing atomic mass, certain sets of properties are found to recur (or at a regular interval)". Since Mendeleev presented his arrangement in a detailed fashion, he is generally given the main credit for putting forward the periodic law.

Lothar Meyer's Scheme : Lothar Meyer illustrated periodic recurrence of properties by plotting atomic volumes (atomic volume = atomic mass/density) against the atomic masses of elements and obtained a curve similar to the one shown in Fig. 5.1. He pointed out that elements occupying similar positions on the peaks and troughs in the curve displayed periodicity in properties. Figure 5.2 is a modern version of Lothar Meyer's curve based on atomic number. On the basis of his curve, Lothar Meyer included 56 elements in his periodic table, arranged in groups and subgroups. Other properties such as fusibility, volatility, malleability, brittleness and electrochemical behaviour, if plotted against atomic mass (or atomic number), yield similar curves.

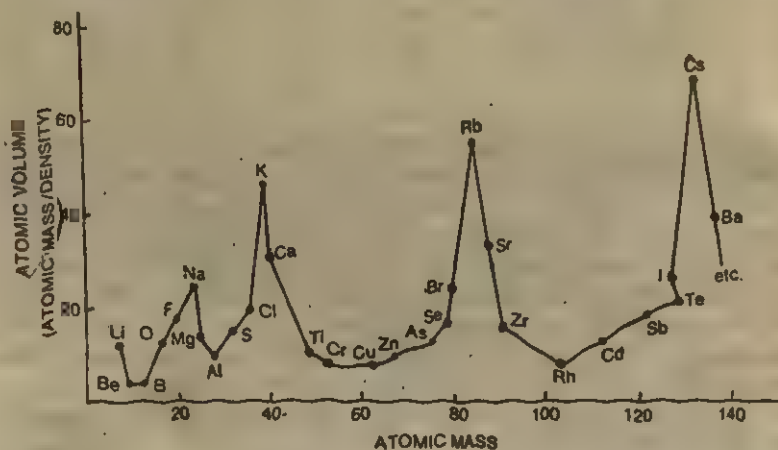


Fig. 5.1 Periodic variation of atomic volume with increasing atomic mass

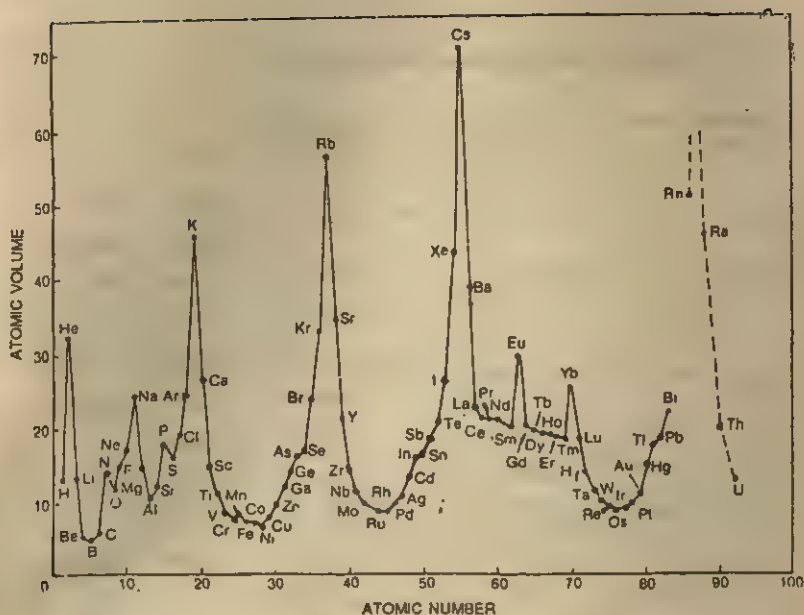


Fig. 5.2 Modern version of Lothar Meyer's curve, i.e., periodic variation of atomic volume with increasing atomic number.

Mendeleev's Periodic Table (Table 5.3): Mendeleev, in his first periodic table (based on Newlands' scheme) published in 1869 (Table 5.3), listed the elements known at that time with related chemical and physical properties in horizontal rows and vertical columns or groups in order of increasing atomic masses.

In a few cases, he challenged the values reported for atomic masses. His challenge was upheld on reinvestigation. For some elements whose correct masses were known, he inverted the sequence (e.g., tellurium $\text{Te}=128$ and iodine, $\text{I}=127$) so that elements with similar properties would be grouped together. To achieve the objective of bringing similar elements into appropriate groups, he left some blank spaces in his table. He predicted that these gaps represented undiscovered elements. Further he suggested that these undiscovered elements would be found to occur in nature along with other members of their family. By considering the properties of their relatives (adjacent elements) he predicted the properties of some of these undiscovered elements that would occupy these gaps after their discovery. Eventually, when these elements were discovered, it was amazing to find that they fitted correctly in his table.

TABLE 5.3 Mendeleev's periodic table published in 1869

			Ti=50	Zr=90	?=180
			V=51	Nb=94	Ta=182
			Cr=52	Mo=96	W=186
			Mn=55	Rh=104,4	Pt=197,4
			Fe=56	Ru=104,4	Ir=198
		Ni=	Co=59	Pd=106,6	Os=199
H=1			Cu=63,4	Ag=108	Hg=200
	Be=9,4	Mg=24	Zn=65,2	Cd=112	
	B=11	Al=27,4	?=68	Ur=116	Au=197,7
	C=12	Si=28	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210
	O=16	S=32	Se=79,4	Te=128?	
	F=19	Cl=35,5	Br=80	I=127	
Li=7	Na=23	K=39	Eb=85,4	Cs=133	Ti=204
		Ca=40	Er=87,6	Ba=137	Pb=207
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		?In=75,6	Th=1		

The element corresponding to the gap between calcium (group II) and titanium (group IV) was named by him as eka-boron (Greek, eka means, 'first after'; because its properties should be similar to that of boron). The two elements for which gaps remained in the table between zinc (group II) and arsenic (group V) were called eka-aluminium and eka-silicon. During the next fifteen years, when these three predicted elements, known as scandium (eka-boron), gallium (eka-aluminium) and germanium (eka-silicon) were discovered, their properties compared very well with those given by Mendeleev. To show the astonishing accuracy of Mendeleev's predictions let us compare the properties of eka-silicon which he predicted in 1871 with those of germanium discovered in Germany by C.A Winkler in 1886 (Table 5.4). Mendeleev published an improved periodic table in 1871 (Table 5.5).

TABLE 5. 4 A comparison of properties predicted by Mendeleev (1871) and reported by Winkler (1886) with those currently accepted for germanium.

Property	Eka-silicon predicted by Mendeleev, 1871	Eka-silicon (germanium) reported by Winkler, 1886	Currently accepted
1 Atomic mass (amu)	72	72.32	72.59
2 Colour	Dark grey	Greyish white	Greyish white
3 Density (g/cm ³)	5.5	5.47	5.35
4 Valence	4	4	4
5 Melting point (K)	High	1231	1222
6 Reaction with water	Will decompose steam with difficulty	Does not decompose water	Does not decompose water
7 Action of acids	Slight	None by HCl or H ₂ SO ₄	Not attacked by HCl or H ₂ SO ₄
8 Action of alkalis	Pronounced	Not attacked by dilute NaOH, dissolved by conc. NaOH	Not dissolved by dilute NaOH, dissolved by conc. NaOH
9 Heating in air Properties of oxide	EsO ₂	GeO ₂	GeO ₂
Physical state	White solid	White solid	White solid
Density (g/cm ³)	4.7	4.703	4.228
10 Compound formed on chlorination Properties of chloride	EsCl ₄	GeCl ₄	GeCl ₄
Physical state	Colourless liquid	Colourless liquid	Colourless liquid
Density (g/cm ³)	1.9 at 273K	1.887 at 291K	1.844
Boiling point (K)	below 373	359	357
11 Compound with sulphur Properties of sulphide	EsS Insoluble in water Soluble in ammonium sulphide	GeS ₂ Insoluble in water Soluble in ammonium sulphide	GeS ₂ insoluble in H ₂ O Soluble in ammonium sulphide
12. Preparation	EsO ₂ + C → Es + C Or Reduction of K ₂ EsF ₆ with Na	GeO ₂ + C → CO ₂ + Ge Or Reduction of K ₂ GeF ₆ with Na	GeO ₂ + C → CO ₂ + Ge

Important Features of Mendeleev's Periodic Table

1. The table is divided vertically into 8 columns known as groups and horizontally into rows known as series. We now call them as periods. These are shown in the Table 5.5

2. The similarities in the properties of the elements within a group are more marked. Basically in arranging the elements he consid-

ered chemical properties, in particular, the ratios in which the elements combine with oxygen or hydrogen. To emphasize this, he put the formula of the group oxide and hydride below the group number in his periodic table.

TABLE 5.5 The Periodic table compiled by Mendeleev (1871)

Period	Series	Group I R_2O	Group II RO	Group III R_2O_3	Group IV RH_4 RO_2	Group V RH_3 R_2O_3	Group VI RH_2 RO_2	Group VII RH R_2O_5	Group VIII RO_4
1	1	H=1							
2	2	Li=7	Be=9.4	B=11	C=12	N=14	O=16	F=19	
3	3	Na=23	Mg=24	Al=27.3	Si=28	P=31	S=32	Cl=35.5	
4	{ 4 5	K=39 (Cu=63)	Ca=40 Zn=65	?=44 ?=68	Ti=48 ?=72	V=51 As=75	Cr=52 Se=78	Mn=55 Br=80	Fe=56 Co=59 Ni=59 Cu=63
5	{ 6 7	Rb=85 (Ag=108)	Sr=87 Cd=112	Yt (y)=88 In=113	Zr=90 Sn=118	Nb=94 Sb=122	Mo=96 Te=125	?=100 I=127	Ru=104 Rh=104 Pd=106 Ag=108
6	{ 8 9 10 11	Cs=133 (-) — (Au=199)	Ba=137 — — Hg=200	La=138 — Er=178 Ti=204	?Ce=140 — ?=180 Pb=207	— — Ta=182 Bi=208	— — W=184 —	— — — —	Os=195 Ir=197 Pt=198 Au=199
7	12	—	—	—	Tl=231	—	U=240	—	

3. He left some blank spaces in his periodic table. Using the properties of the element located around the blank positions he predicted the properties of some undiscovered elements that would occupy the blank spaces after their discovery.

4. Isotopes were not given separate places even though they had different atomic masses.

5. The table was helpful in establishing the valency (group number of elements correspond to their valencies) and atomic masses of elements. Element beryllium for a long time was considered to be an analogue of aluminium and its oxide was assumed to have the formula Be_2O_3 . Atomic mass of beryllium was known to be 13.5 on the basis of its properties. Mendeleev had placed it in 2nd group above magnesium. So its oxide must have the formula BeO . On this basis the atomic mass of beryllium was found to be nine which was confirmed soon after. Its atomic mass was corrected later. Thus, by placing the elements strictly according to the similarities in the properties, Mendeleev was able to correct certain atomic masses.

6. Some elements appeared to be out of place in the periodic table on the basis of accepted values for their atomic masses, *i.e.*, elements with higher atomic masses preceded those with lower atomic masses. Mendeleev placed such elements (Ar and K; Te and I; Co and Ni) in locations consistent with their properties, and attributed the apparent reversal of atomic masses to their incorrect values. Later these values were found to be correct.

The periodic table has been modified, since mendeleev first formulated it, to give an improved interpretation of the chemistry of the elements. In these improved versions of the table, the basic format has been retained which is an indication of its acceptability as a basis of discussion of the chemistry of the elements. A periodic table based on Mendeleev's 1871 table is shown in Table 5.6. Each group of the table has been divided into two sub-groups 'A' and 'B'. The resemblances in the properties of the elements within a sub-group are more marked than those between members of the two sub-groups. In the table, under the head of zero group, inert gases have been placed not discovered in 1871. These gases could not be foreseen by Mendeleev as he did not leave any space for them. The first inert gas was discovered in 1894 by Rayleigh and Sir William Ramsay.

TABLE 5.6 : A periodic table based on Mendeleev's table of 1871. The circles indicate elements not known in 1871. Table gives the currently accepted values of atomic masses. Numbers in parentheses are the mass numbers of the most stable isotopes

I B		II B		III B		IV B		V B		VI B		VII B		VIII B		0	
H 1.0																	H ₄ 4.0
Li 6.9		Be 9.0		B 10.8		C 12.0		N 14.0		O 16.0		F 19.0					Ne 20.2
Na 23.0		Mg 24.3		Al 27.0		Si 28.1		P 31.0		S 32.1		Cl 35.5					Ar 39.9
K 39.1		Ca 40.1	Sc (45.0)	Ti 47.9		V 50.9		Cr 52.0		Mn 54.9		Fe 55.8	Co 58.9	Ni 58.7			
	Cu 63.5	Zn 65.4	Ga (69.7)		Ge (72.6)	As 74.9		Se 79.0		Br 79.9							Kr (83.8)
Rb 85.5		Sr 87.6	Y 88.9	Zr 91.2		Nb 92.9		Mo 95.9		Tc (98.9)		Ru 101.1	Rh 102.9	Pd 106.4			
	Ag 107.9	Cd 112.4	In 114.8		Sn 118.7	Sb 121.8		Te 127.6		I 126.9							Xe (131.3)
Cs 132.9		Ba 137.3	La* 138.9	Hf (178.5)		Ta 180.9		W 183.8		Re (186.2)		Os 190.2	Ir 192.2	Pt 195.1			
	Au 197.0	Hg 200.6		Tl 204.4		Pb 207.2		Bi 209.0		Po (210)		At (210)					Rn (222)
Fr (223)		Ra (226.0)	Ac (227)														
Ce 140.1	Pr 142.9	Nd 144.2	Pm (147)	Sm 150.4	Eu 152.0	Gd 157.3	Tb 158.9	Dy 162.5	Ho 164.9	Er 167.3	Tm 168.9	Yb 173.0	Lu 175.0				
Th 232.0	Pa 231.0	U 238.0	Np 237	Pu (242)	Am (243)	Cm (247)	Bk (247)	Cf (251)	Es (254)	Fm (253)	Md (258)	No (259)	Lr (262)				

The modern periodic table is essentially similar to that of Mendeleev. A new column has been added to accommodate noble gases which were discovered around 1900. At a time when nothing was known about atomic structure, Mendeleev gave this rational classification of element. This classification through the years has facilitated the correlation of new informations. With the discovery of electron and Moseley's determination of atomic number from X-ray spectra of the elements a new basis of classification emerged. It is now based on atomic number (related to increasing nuclear charge) rather than atomic mass. Later, in this unit, we shall see how the electronic configuration of atoms provides a fundamental basis for the periodic classification of elements.

5.4 MODERN BASIS OF CLASSIFICATION

The periodic table has been modified from time to time since Mendeleev first formulated it. Additional elements have been added as they were discovered. The very basis upon which the periodic table was founded has been changed. Mendeleev believed that the periodicity was a function of atomic mass. Now with the determination of atomic numbers by Henry Moseley* (1913), it was realized that the atomic number of an element is a more fundamental feature than its atomic mass and accordingly the periodic law advanced by Mendeleev was changed. Thus, today periodicity is based upon atomic number, not atomic mass. Mendeleev could not possibly have reached this conclusion since the electron and proton were not discovered until 1897 and 1902 respectively and atomic numbers were not known until 1913.

The modern periodic law proposed by Moseley states that the properties of the elements are periodic function of their atomic numbers.

Accordingly, the problem of accommodating the isotopes could be satisfactorily solved by keeping them in one place only (isotopes have the same atomic number). The introduction of atomic number also explained certain difficulties seen in connection with atomic masses in the Mendeleev's table. The anomaly of placing argon before potassium is solved as the atomic number of argon is 18 and that of potassium is 19. The inversions of iodine and tellurium; and nickel and cobalt could also be thus explained.

It has now been realized that the atomic number dictates the number of electrons in an atom. Electronic structures of the atoms of

* Henry Moseley, in 1913, bombarded some metals with high speed electrons in a cathode ray tube. It was observed that X-rays so produced were characteristic for each element. Moseley further observed that the wavelengths of the characteristic peaks in the X-ray spectra were related to interpret his finding by concluding that the atomic number is a measure of the positive charge in the atomic nucleus. The atomic number then, becomes a much more fundamental quantity than the atomic mass.

the elements vary periodically with atomic number. Thus, the periodic recurrence of similar electronic configuration leads to a periodic recurrence in chemical properties also.

A more satisfactory statement of the periodic law can thus be arrived at as given below :

“Since the electronic structure of atoms of the elements varies periodically with atomic number, all elemental properties dependent on atomic structure also tend to vary periodically with atomic number”.

5.5 THE MODERN PERIODIC TABLE - THE LONG FORM

Over the years, the periodic table has taken a variety of forms. There has been the short form, the long form, spiral table, three dimensional helical table and a number of others. The periodic table, the most commonly accepted and used today, is a version of the long form. Classification of elements in the long form of periodic table is based on their electronic configurations. The elements are arranged in the increasing order of atomic numbers so that the facts described by the periodic law are efficiently organized. Firstly, all those elements that are most similar get placed in the same vertical column. Secondly, elements get arranged in an orderly manner in periods and present the transition from beginning to the end of period.

The periodic table provides a valuable framework for organizing and systematizing the study of elements and their compounds. It has been found that periodic recurrence of similar electron configurations leads to a periodic recurrence of chemical properties. In other words, it can be expressed that the chemical as well as physical properties of the elements are related to their electronic structures. It is not possible to explain all the characteristics known of the elements from their electronic configurations. However, from this classification one can correlate many experimentally observed properties with electronic configurations. One can understand the causes of periodicity in properties and general trends in the behaviour of elements. The salient features of the periodic table are illustrated through the Table 5.7.

The vertical columns which bring together similar elements are called groups or families. There are 18 groups which are numbered 1-18 in accordance with the 1984 IUPAC recommendations. The system replaces the old numbering scheme using Roman numerals (*i.e.*, from I to VIII), Zero and English alphabet (A and B for dividing one group into A and B, *e.g.*, IA, IIB, *etc.*)

The horizontal rows of the table are called periods. There are seven periods in all. Each period is numbered by the number of the outermost energy level of the atoms in which the electrons are gradually filled as the atomic number increases. For example, the electronic

Representative
elements

d-transition elements

Representative elements

Noble

GROUP 1

TABLE 5.7 Long form of the Periodic Table of the Elements with their atomic number and ground state electronic configurations. The groups are numbered 1 - 18 in accordance with the 1984 IUPAC recommendations. This notation replaces the old numbering scheme of IA - VIIA, of IB - VII B and VIII for s,p, and d block elements.

PERIOD NUMBER	GROUP 1		GROUP NUMBER										GROUP NUMBER					GROUP 18
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	2
1	H 1s ¹																	He 1s ²
2	Li 2s ¹	Be 2s ²											B 2s ² 2p ¹	C 2s ² 2p ²	N 2s ² 2p ³	O 2s ² 2p ⁴	F 2s ² 2p ⁵	Ne 2s ² 2p ⁶
3	Na 3s ¹	Mg 3s ²											Al 3s ² 3p ¹	Si 3s ² 3p ²	P 3s ² 3p ³	S 3s ² 3p ⁴	Cl 3s ² 3p ⁵	Ar 3s ² 3p ⁶
4	K 4s ¹	Ca 4s ²	Sc 3d ¹ 4s ²	Ti 3d ² 4s ²	V 3d ³ 4s ²	Cr 3d ⁵ 4s ¹	Mn 3d ⁵ 4s ²	Fe 3d ⁶ 4s ²	Co 3d ⁷ 4s ²	Ni 3d ⁸ 4s ²	Cu 3d ¹⁰ 4s ¹	Zn 3d ¹⁰ 4s ²	Ga 4s ² 4p ¹	Ge 4s ² 4p ²	As 4s ² 4p ³	Se 4s ² 4p ⁴	Br 4s ² 4p ⁵	Kr 4s ² 4p ⁶
5	Rb 5s ¹	Sr 5s ²	Y 4d ¹ 5s ²	Zr 4d ² 5s ²	Nb 4d ⁴ 5s ¹	Mo 4d ⁵ 5s ¹	Tc 4d ⁵ 5s ²	Ru 4d ⁷ 5s ¹	Rh 4d ⁸ 5s ¹	Pd 4d ¹⁰	Ag 4d ¹⁰ 5s ¹	Cd 4d ¹⁰ 5s ²	In 5s ² 5p ¹	Sn 5s ² 5p ²	Sb 5s ² 5p ³	Te 5s ² 5p ⁴	I 5s ² 5p ⁵	Xe 5s ² 5p ⁶
6	Cs 6s ¹	Ba 6s ²	La ^a 5d ¹ 6s ²	Hf 4f ¹⁴ 5d ² 6s ²	Ta 4f ¹⁴ 5d ³ 6s ²	W 5d ⁴ 6s ²	Re 5d ⁵ 6s ²	Os 5d ⁶ 6s ²	Ir 5d ⁷ 6s ²	Pt 5d ⁹ 6s ¹	Au 5d ¹⁰ 6s ¹	Hg 5d ¹⁰ 6s ²	Tl 6s ² 6p ¹	Pb 6s ² 6p ²	Bi 6s ² 6p ³	Po 6s ² 6p ⁴	At 6s ² 6p ⁵	Rn 6s ² 6p ⁶
7	Fr 7s ¹	Ra 7s ²	Ac ^{a*} 6d ¹ 7s ²	Unq	Unp	Unh	Uns											

f-inner transition elements

^a Lanthanides
4fⁿ5d⁰⁻¹6s²

^{a*} Actinides
5fⁿ6d⁰⁻¹7s²

58 Ce 4f ¹ 5d ¹ 6s ²	59 Pr 4f ³ 5d ⁰ 6s ²	60 Nd 4f ⁴ 5d ⁰ 6s ²	61 Pm 4f ⁵ 5d ⁰ 6s ²	62 Sm 4f ⁶ 5d ⁰ 6s ²	63 Eu 4f ⁷ 5d ⁰ 6s ²	64 Gd 4f ⁷ 5d ¹ 6s ²	65 Tb 4f ⁹ 5d ⁰ 6s ²	66 Dy 4f ¹⁰ 5d ⁰ 6s ²	67 Ho 4f ¹¹ 5d ⁰ 6s ²	68 Er 4f ¹² 5d ⁰ 6s ²	69 Tm 4f ¹³ 5d ⁰ 6s ²	70 Yb 4f ¹⁴ 5d ⁰ 6s ²	71 Lu 4f ¹⁴ 5d ¹ 6s ²
90 Th 5f ⁰ 6d ² 7s ²	91 Pa 5f ² 6d ¹ 7s ²	92 U 5f ³ 6d ¹ 7s ²	93 Np 5f ⁴ 6d ¹ 7s ²	94 Pu 5f ⁶ 6d ⁰ 7s ²	95 Am 5f ⁷ 6d ⁰ 7s ²	96 Cm 5f ⁷ 6d ¹ 7s ²	97 Bk 5f ⁹ 6d ⁰ 7s ²	98 Cf 5f ¹⁰ 6d ⁰ 7s ²	99 Es 5f ¹¹ 6d ⁰ 7s ²	100 Fm 5f ¹² 6d ⁰ 7s ²	101 Md 5f ¹³ 6d ⁰ 7s ²	102 No 5f ¹⁴ 6d ⁰ 7s ²	103 Lr 5f ¹⁴ 6d ¹ 7s ²

configuration of chlorine (2, 8, 7) suggests that this is an element from period 3, because chlorine's outermost shell number 3 is still incomplete.

Today's quantum mechanical picture of the electronic structure of the atom fits directly into the periodic table and indeed explains the periodicity observed. Each period represents a principal quantum number. Each successive period in the periodic table is associated with the filling of next higher principal energy level (*i.e.*, $n=1$, $n=2$, *etc.*). Each period will accommodate elements as dictated by the numbers of atomic orbitals. Thus, the number of elements will always be twice the number of atomic orbitals as one orbital can accommodate two electrons. So, the first period has two elements—hydrogen ($1s^1$) and helium ($1s^2$); and the second period has eight—lithium ($2s^1$), beryllium $2s^2$, boron ($2s^2, 2p^1$)... and neon ($2s^2 2p^6$). The third period contains eight elements (from Na to Ar) because in the aufbau process the 3d orbitals do not fill until after the 4s orbital. Each successive group from left to right represents one more electron in the principal energy level. Thus, not surprisingly, the periodic arrangement relates to the aufbau process as regard to the electronic configuration of the elements.

Periods are sometimes called short and long periods, depending upon the number of elements. The first period is called very short period. The second and third periods are called short periods.

The fourth and fifth periods have 18 elements each. They are called long periods. These two periods also include transition elements. The sixth period with 32 elements is called very long period. It includes 14 rare earth elements from atomic number 58 to 71 (lanthanides). They all are placed in one box because of similar properties. The 7th period is incomplete having 21 elements and is also called a very long period. It includes elements from atomic number 90 to 103 (actinides). Similar to lanthanides, they are also placed in one box. With the help of the periodic table we can determine the ground state electronic structure of an element almost at a glance.

5.6 TYPES OF ELEMENTS

From the aspect of electronic configuration, the periodic table is divided into four major groups or blocks or elements showing the highest occupied orbital in an atom. Table 5.7 shows such a division into the s, p, d and f orbital blocks. The blocks are also named after the general characteristics of the elements. For example, s (groups 1, 2) and p-blocks (groups 13 to 18), the main groups consist of the active metals and non-metals respectively (the p-block also contains some metals). Elements constituting these two blocks are called **representative elements**. The d-block (groups 3 to 12) is called the 'transition block' since its properties are intermediate - between those of the two main blocks. The f-block elements are described as 'inner-transition elements'.

Sometimes groups are designated by names : group 1 elements (excluding H) are called the alkali metals ; group 2 elements are called the alkaline earth metals ; the elements of group 17 are called halogens; and those of group 0 (18) are the inert or noble gases (Fig. 5.3).

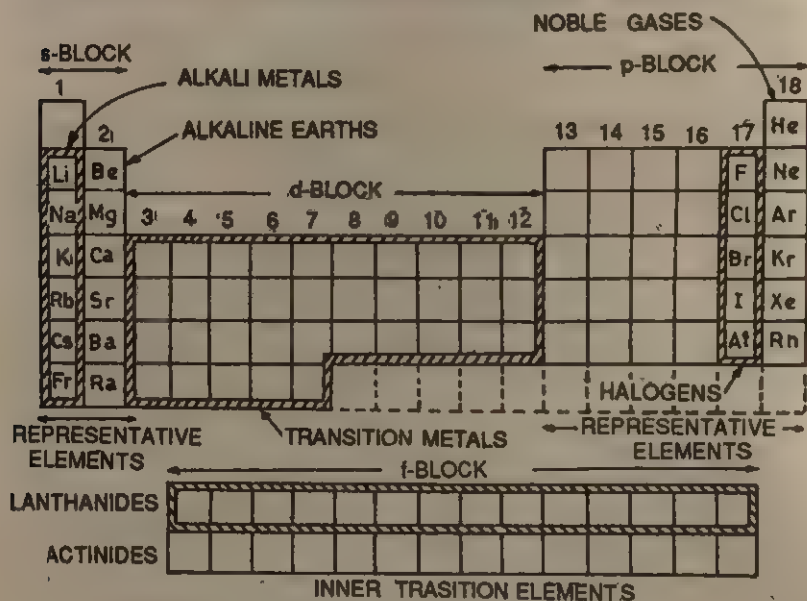


Fig. 5.3 Different groups of elements

In group 3, fourteen extra elements are placed along with lanthanum and the same number of extra elements are kept with actinium. They are called 'lanthanides' and actinides' and are placed separately outside the body of the table. They are called inner-transition elements.

5.6.1 Noble Gases

The noble gases are found at the end of each period in group 18 of this periodic table.

All noble gases except helium have the stable outer electronic configurations $ns^2 np^6$. Helium has the $1s^2$ configuration. The stable electronic configuration well explains for their high degree of chemical inertness in common chemical reactions. This configuration is also associated with inertness for ionized elements, e.g., Na^+ , Ca^{2+} , Al^{3+} , etc., and is the basis of the octet rule. Only a few compounds of Xe and Kr have been prepared. They are monoatomic gases with low melting and boiling points.

5.6.2 Representative Elements (s and p-block elements)

s-block elements : The first two groups of elements, i.e., 1 (alkali metals ; Li....Fr) and 2 (alkaline earth metals Be...Ra) are placed in s-block. In these elements, s orbital of the outermost energy level is filled up with electrons. Their outermost electronic configuration is ns^1

and ns^2 . All these elements form colourless ions and they react readily with diluted acids or water liberating hydrogen.

p-block elements : The elements of groups 13 to 17 (electronic configuration varying from $ns^2 np^1$ to $ns^2 np^5$) as well as the group 18 elements on the extreme right of the periodic table (He.....Rn), are placed in the p-block. Their atoms tend to gain electrons to form negative ions. It includes a very reactive group of elements, i.e., halogens. Most of them are non-metals.

Elements of s and p-block (excluding noble gases) acquire noble gas configuration in the course of chemical compounds formation. Elements of s and p-blocks are often called **representative elements**. Their chemistry is determined by the number of electrons in the outermost shell called the valence shell. The number of valence electrons for s-block is the same as the group number ; for p-block (groups 13-17 only) the number of valence electrons is obtained by subtracting 10 from the group number. Across each period, the elements acquire from metallic to non-metallic nature.

5.6.3 Transition Elements (d-block elements)

This block includes the transition elements which form a bridge between s and p-block elements. Elements of groups 3, 4, 5.... to 12 with general electronic configuration $(n-1)d^{1-10} ns^{0-2}$ belong to d-block. For these elements the inner d orbital is progressively filled up with electrons as the atomic number increases. Thus, atoms or ions of these elements contain incomplete d orbital. They are all metals. These elements form coloured ions of different oxidation states. They have a strong tendency to form complex compounds.

5.6.4 Inner-Transition Elements (f-Block elements)

Elements with atomic numbers 58-71 (lanthanides) and 90-103 (actinides) are those in which 4f and 5f orbitals are incomplete. These are called inner-transition elements. Their general electronic configuration is $(n-2)f^{1-14} (n-1)d^{0-10} ns^{0-2}$. They also have incomplete $(n-1)$ d orbital. Their outstanding property is their very close similarity in chemical behaviour. These elements constitute two separate rows below the body of the periodic table - one of lanthanides and other of actinides.

5.7 PERIODIC PROPERTIES - THE PERIODIC TABLE

It is a matter of general experience that atoms with similar outershell electronic configuration have similar chemical properties, hence, if one can arrange all known atoms in some systematic fashion according to their electronic structures, periodic recurrence in chemical properties would be evident. For example, both F and Cl with seven electrons in their outermost shell combine with hydrogen and sodium to form similar compounds, e.g., HF(g), HCl(g), NaF(s), NaCl(s).

Many characteristic atomic properties depend upon electronic configuration / atomic number, and thus, show periodic variation. We will now discuss some of these properties and see how this periodic variation takes place within the periodic table.

Periodic Trends in Properties of Elements

5.7.1 Valence (or Valency)

The electrons occupying the outermost shell are referred to as valence electrons, which in turn determine the valency of an element.

The valence of an element can be inferred from its position in the periodic table. The valence of representative elements is usually equal to the number of electrons in the outermost orbitals and/or equal to eight minus the number of electrons in the outermost orbital. For example, elements belonging to groups 1, 2, 13 and 14 exhibit valencies 1, 2, 3 and 4 respectively in combination with hydrogen. Elements from groups 15, 16 and 17 show trivalency, bivalency and monovalency respectively in combination with hydrogen and chlorine (Table 5.8). On the other hand, elements from groups 1, 2, 13 to 17 show valencies 1 to 7 in combination with oxygen (Table 5.9).

Transition elements exhibit variable valency but all of them exhibit a common valency of 2.

In a group, all the member elements show the same valency in combining with other elements. For example, the formation of HF from fluorine and hydrogen (one fluorine atom combines with one hydrogen atom) enables one to predict that chlorine and other group 17 elements also form compounds with hydrogen in the atomic ratio of 1 : 1 (HCl, HBr, HI). This relationship is further illustrated in Table 5.10.

TABLE 5.8 Valence electrons and valency with respect to hydrogen and chlorine for the first short period elements

Property	Li	Be	B	C	N	O	F
Group	1	2	13	14	15	16	17
Valence electrons	1	2	3	4	5	6	7
Valency with respect to hydrogen and chlorine	1	2	3	4	3	2	1
Examples:							
Hydride	LiH	BeH ₂	BH ₃ (B ₂ H ₆)	CH ₄	NH ₃	OH ₂ (H ₂ O)	FH (HF)
Chloride	LiCl	BeCl ₂	BCl ₃	CCl ₄	NCl ₃	OCl ₂ (Cl ₂ O)	FCl (ClF)

TABLE 5.9 Valence electrons and valency with respect to oxygen for the second short period elements

Property	Na	Mg	Al	Si	P	S	Cl
Group	1	2	13	14	15	16	17
Valence electrons	1	2	3	4	5	6	7
Valency with respect to oxygen	1	2	3	4	5	6	7
Example : Oxide	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅ P ₄ O ₁₀	SO ₃	Cl ₂ O ₇

TABLE 5.10 Formulae of compounds of hydrogen with elements of representative groups

Group	1	2	13	14	15	16	17
Group valency with hydrogen	1	2	3	4	3	2	1
	LiH NaH KH RbH CsH	BeH ₂ MgH ₂ CaH ₂ SrH ₂ BaH ₂	BH ₃ (B ₂ H ₆) AlH ₃ GaH ₃ InH ₃ TlH ₃	CH ₄ SiH ₄ GeH ₄ SnH ₄ PbH ₄	NH ₃ PH ₃ AsH ₃ SbH ₃ BiH ₃	H ₂ O H ₂ S H ₂ Se H ₂ Te H ₂ Po	HF HCl HBr HI

Mendeleev had used the formulae of oxides and hydrides formed by the elements as a basis for classifying the elements into groups and periods.

5.7.2 Atomic Radius (Size) of Atoms and Ions

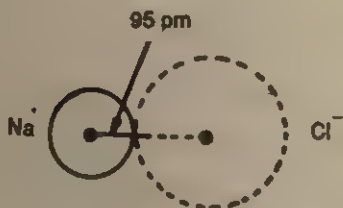
Atoms and ions possess no finite size owing to uncertainty in the position of orbiting electrons around the nucleus. However, the size of an atom can be estimated from its atomic radius which is defined as the most probable distance from the nucleus to a point where the electron density is effectively zero (negligible). To measure the atomic radius the distance between the nuclei of two adjacent atoms in a molecule is determined spectroscopically. One half of internuclear distance gives the atomic radius for a homonuclear diatomic molecule, *e.g.*, the bond distance in the hydrogen molecule (H₂) is 74 pm and half of this distance (37 pm) is taken as the atomic radius. For non-metallic atoms, the term 'atomic radius' is adopted to define the radius or size of the atom bound by a single covalent bond (Fig. 5.4).

In case of metals, atomic radius is defined as half of the inter-nuclear distance between the two adjacent metal ions in the metallic crystal (Fig. 5.4).

COVALENT RADIUS:



IONIC RADIUS:



METALLIC RADIUS:

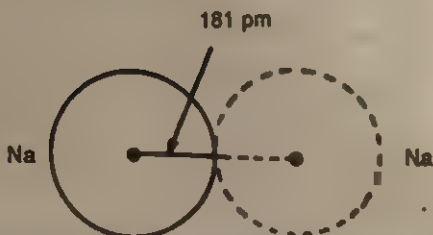


Fig. 5.4 A comparison of covalent, ionic and metallic radii. 1. The covalent radius is one half the distance between the centres of two Na atoms in the gaseous molecule, $\text{Na}_2(\text{g})$. 2. The ionic radius is based on the distance between centres of ions in an ionic compound, for example, NaCl . Here, of course, the cation and anion are of different sizes. 3. The metallic radius is taken as one half the distance between the centres of adjacent atoms in solid metallic sodium.

In general, the size of the atom gradually decreases as we proceed from left to right across a period in the periodic table (Figs. 5.5, 5.6, 5.7 and 5.8). This is because of the increasing nuclear charge while the electrons are added to the same shell. Due to an increase in the nuclear charge, the electrons are attracted toward the nucleus to a great extent, and thus, atomic radius decreases. But the inert gases at the end of periods do not follow suit because of their complete valence shells. Electrons within the valence shell repel one another. As a result, the electron cloud expands, and thus, size increases (Table 5.11).

On the other hand the size of the atom generally increases as we move down within a group (Figs. 5.5, 5.9, 5.10, 5.11, 5.12 and 5.13; Tables 5.12 and 5.13). This trend is expected as it corresponds to the

addition of electrons in successive energy levels. Although the nuclear charge increases, the net effect of additional new energy shell is very large and outweighs the contractive effect of the increased nuclear charge. Electrons in the lower energy levels shield the outermost electrons from the attraction of positively charged nucleus. Thus, the effective nuclear charge experienced by the outermost electrons depends on the extent to which these electrons are screened from the nucleus.

Figure 5.14 shows the variation of the atomic radii of the elements with atomic number. The alkali metals occupy the maxima of the plot, and the halogens and noble gases (Kr, and Xe) atoms occupy minima. Atomic sizes of He, Ne and Ar are not available because any molecule containing these atoms is hardly known.

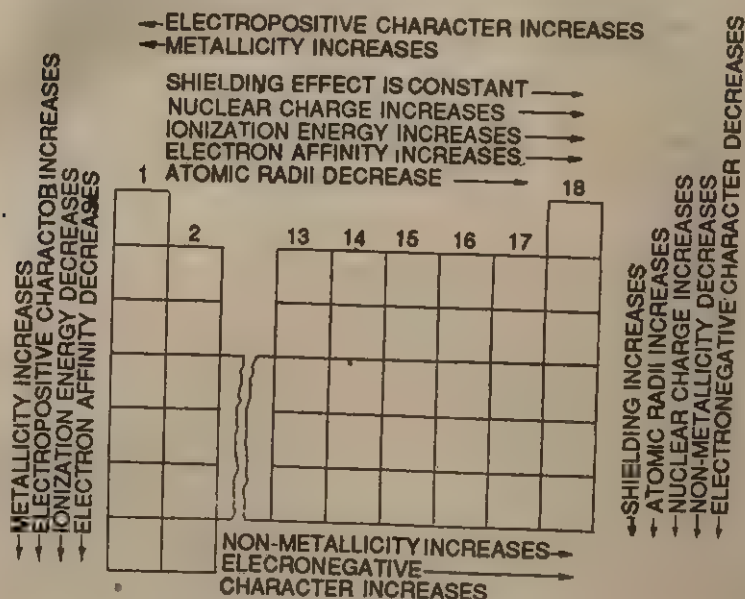


Fig. 5.5 Some periodic trends increasing in the direction of arrows

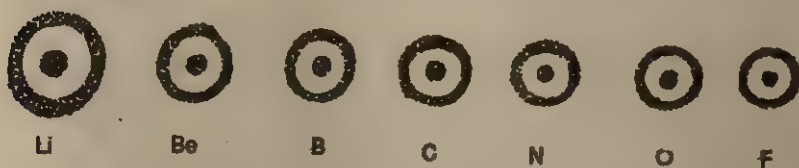


Fig 5.6 Representation of the trends in atomic sizes of the second row elements showing the electron shells.

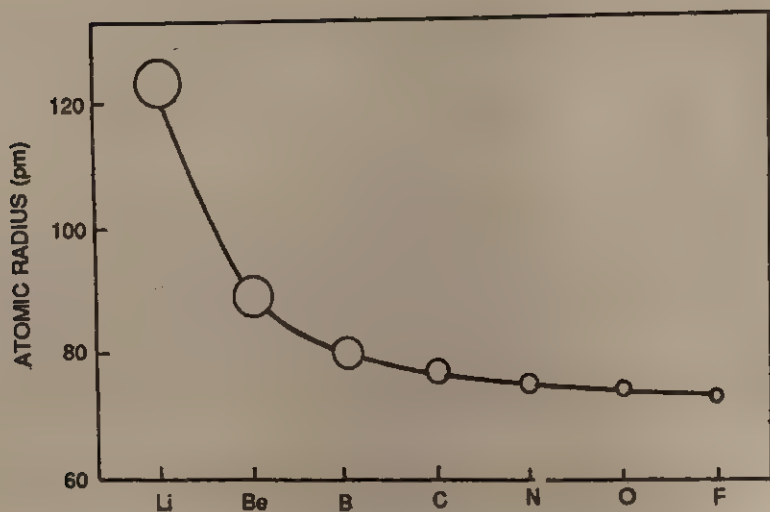


Fig.5.7 Trends in atomic radii of the 2nd period elements (atomic radius decreases from Li to F)

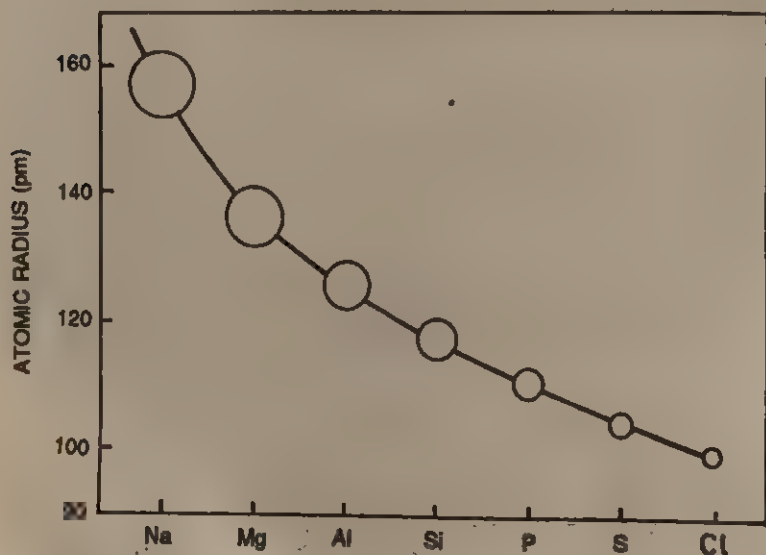


Fig.5.8 Trends in atomic radii of 3rd period elements (atomic radius decreases from Na to Cl)



Fig. 5.9 Representation of trends in the atomic sizes of the alkali metals showing the electron shells.

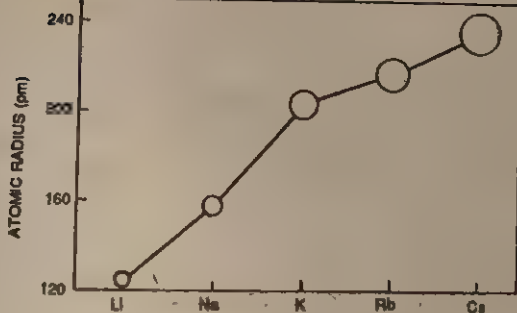


Fig. 5.10 Trends in atomic radii of alkali metals (atomic radius increases from Li to Cs)

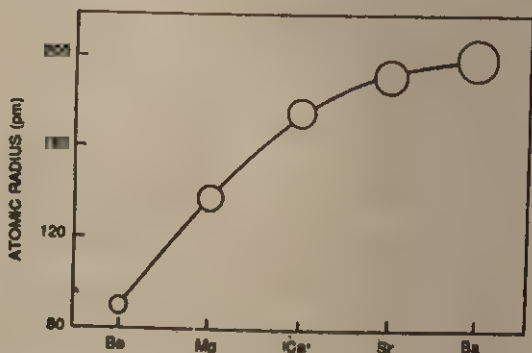


Fig. 5.11 Trends in atomic radii of alkaline earth metals (atomic radius increases from Be to Ba)

5.7.3 Density, Melting Point and Boiling Point

Elements show periodic variation for these properties also. For example, if we consider the periods of representative elements, we observe that densities (Table 5.11), melting and boiling points (Table 5.11) of elements increase across the period and reach a maximum value in the middle of the series. It can be realized from Fig. 5.15 that

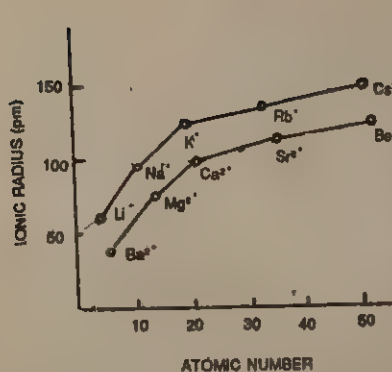


Fig. 5.12 Trends in ionic radii for alkali and alkaline earth metals

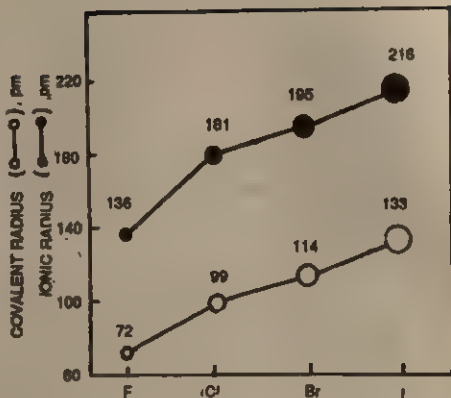


Fig. 5.13 Atomic (covalent) and ionic radii of the halogen family

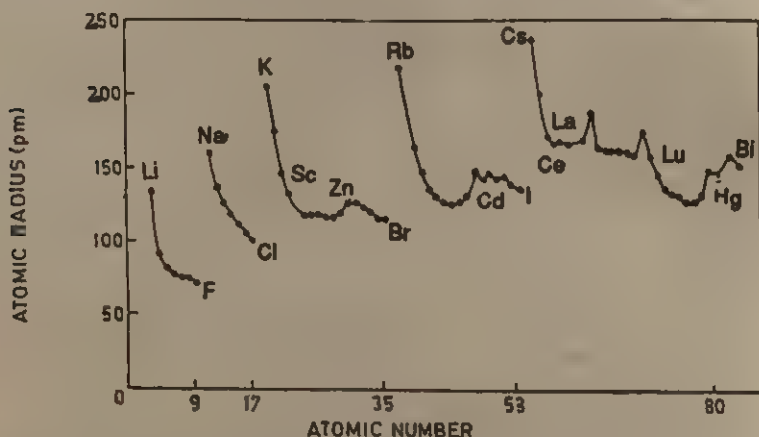


Fig. 5.14 Periodic variation in atomic (or covalent) radii. The largest atoms in any period are the alkali metals

carbon (in the middle of second period) and silicon (in the middle of third period) have the highest melting points in periods 2 and 3 respectively. Similarly transition elements also attain the highest values for these properties in the middle of the series.

A general gradation in these properties is also observed in a periodic group. Generally densities increase while melting and boiling points decrease in moving down the group (Tables 5.12 and 5.13; Figs. 5.16, 5.17, 5.18 and 5.19)

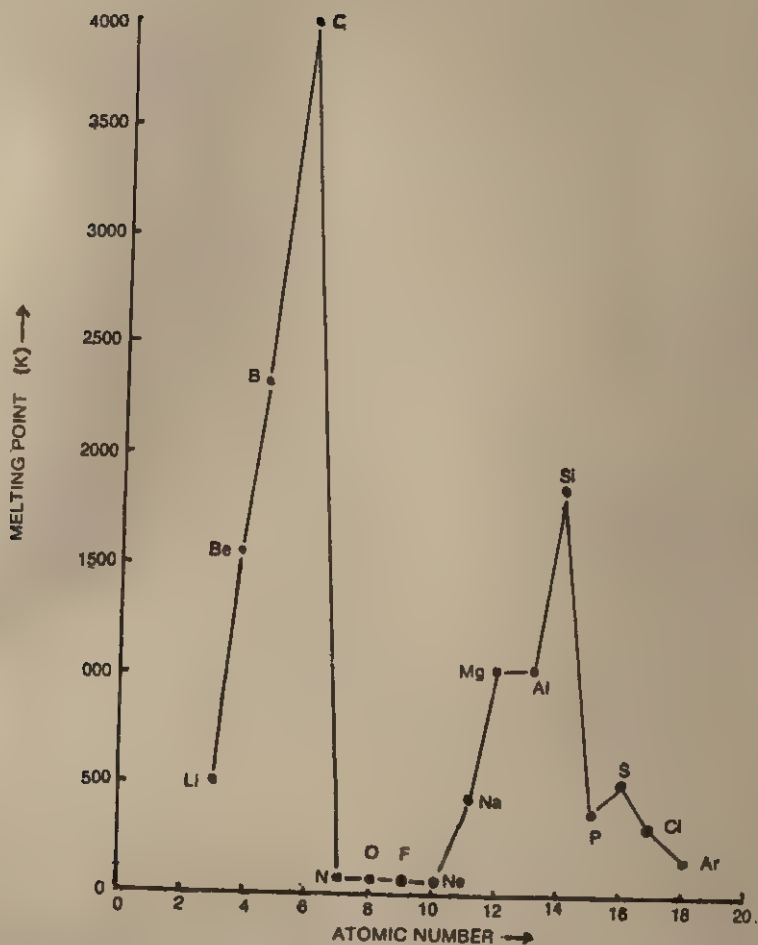


Fig.5.15 Melting points of the elements versus their atomic numbers.

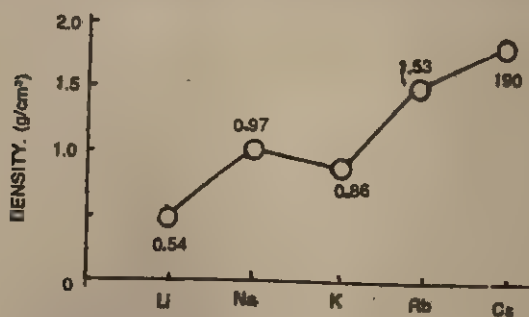


Fig.5.16 Trends in densities of alkali metals

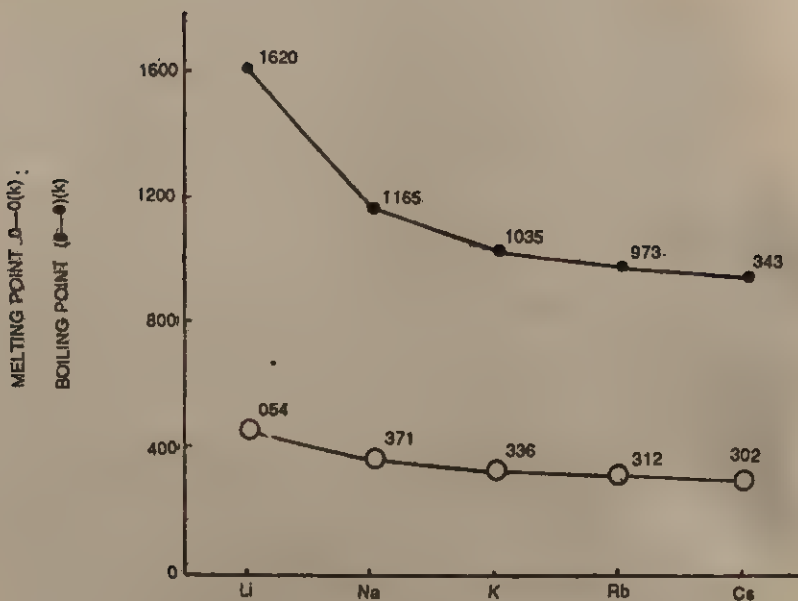


Fig.5.17 Trends in melting and boiling points of alkali metals

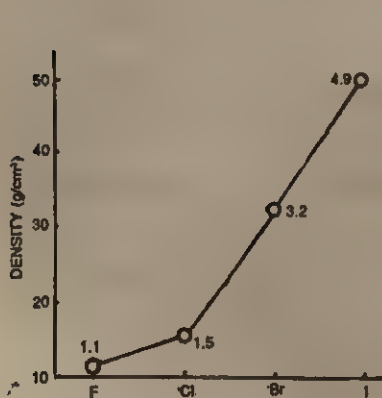


Fig.5.18 Trends in densities of halogens

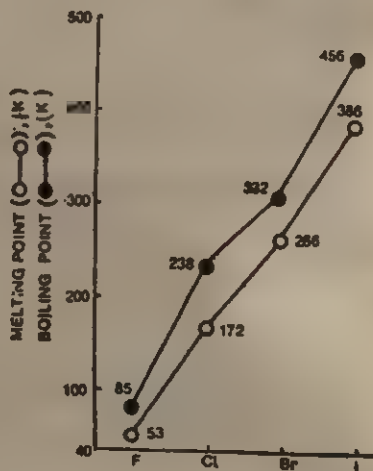


Fig.5.19 Trends in melting and boiling points of halogens

TABLE 5.11 Densities, atomic sizes, melting and boiling points of the second and third period elements.

Elements of second period	Li	Be	B	C	N	O	F	Ne
Density(g/cm ³)	0.54	1.86	2.34	3.51 (diamond) 2.22 (graphite)	0.87	1.14	1.11	
Atomic size(pm)	123	89	80	77	75	74	72	154
Melting point (K)	454	1550	2273	3800	63.2	54.6	53	24.4
Boiling point (K)	1620	2733	2823	4473	77.2	90	85	27.2
Elements of third period	Na	Mg	Al	Si	P		Cl	Ar
Density(g/cm ³)	0.97	1.75	2.70	2.33	1.82 (white)	1.7 (rhombic)	1.50	
Atomic size(pm)	157	136	125	117	110	104	99	104
Melting point (K)	371	924	933	1683	313	392	172	84
Boiling point (K)	1165	1380	2740	2628	553	718	238.4	87

TABLE 5.12 Physical properties of alkali metals

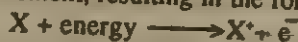
Alkali metal	Atomic number	Atomic radius, pm	Density g/cm ³	Melting point, K	Boiling point, K
Li	3	123	0.54	454	1620
Na	11	157	0.97	371	1165
K	19	203	0.86	336	1047
Rb	37	216	1.53	312	961
Cs	55	235	1.87	302	951

TABLE 5.13 Physical properties of halogens

Halogen	Atomic number	Atomic radius, pm	Density g/cm ³	Melting point, K	Boiling point, K
F	9	72	1.1	53	85
Cl	17	99	1.5	172	238
Br	35	114	3.2	266	332
I	53	133	4.9	386	456

5.7.4 Ionization Energy

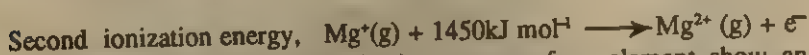
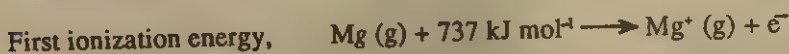
It is the minimum amount of energy required to remove the most loosely bound electron from one mole of gaseous atoms (isolated atoms) of an element, resulting in the formation of a positive ion.



(Gaseous atom) (Gaseous ion)

The process which corresponds to the above equation is called the first ionization energy of X, and is expressed in kilo joules per mole (kJ mol⁻¹) of atoms of X.

Thus, the energy required to remove the second electron from X^+ is termed the second ionization energy, and so on. Generally, the second ionization energy is higher than the first, e.g.,



Successive values of ionization energy of an element show an increasing trend. This trend is expected as the species from which the electron is removed becomes progressively more positively charged. The attraction between the positive ion and the electron is stronger than between the neutral atom and the electron.

The variation of the first ionization energy across the periods and down the groups, illustrated in Fig. 5.20, parallels quite closely the trends in atomic size. This really should not be too surprising since the ionization energy of an atom should depend upon the distance of the electron from the nucleus. In addition, it should also depend upon the magnitude of nuclear charge and the shielding effect of the inner electrons.

Thus, we find that the ionization energy decreases on descending a group because the force with which a nucleus attracts an electron drops off rapidly as the distance between the electron and the nucleus increases. Additionally, the decrease is due to the fact that filled sets of inner orbitals screen the positively charged nucleus from the outermost electrons, which therefore, are not strongly held.

As we move across a period, an increasing amount of energy is required to remove an electron from the outermost (valence) shell. The increase is due to the fact that the force of attraction between positively charged nucleus and electrons increases because the added electrons while occupying the same shell experience the increased nuclear charge which causes the shell to shrink in size. Additionally, the filled sets of inner orbitals shield the nucleus from the outermost electrons to a small extent as the building up of the atom with increasing atomic number takes place in the same shell. Thus, the larger effective nuclear charge and smaller size make removal of the electron more difficult.

Effective nuclear charge : The ease with which the outer electron is removed from an atom is governed by the extent to which it is influenced by the positively charged nucleus. Owing to shielding provided by the inner electrons in an atom, the valence electron does not experience the nuclear charge fully (corresponding to the atomic number, Z) but an effective nuclear charge, Z^* ($Z^* = Z - S$, where S = shielding effect). Electrons in the same subshell (subshell from which electron is to be removed) also shield each other to a small extent. This adds to the shielding afforded by the inner

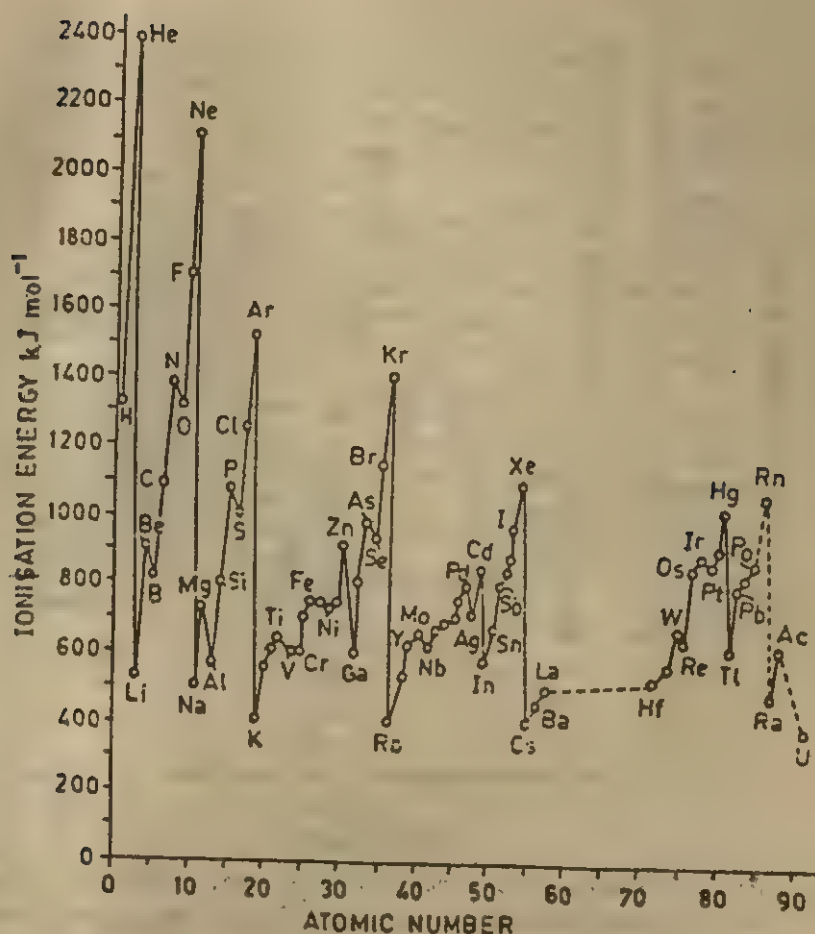


Fig.5.20 Variation of first ionization energy with atomic number

electrons. It is also responsible for the overall increase in ionization energy which occurs within each period (within group also).

Figure 5.21 shows the non-uniform increase in ionization energy that occurs on traversing the first two short periods. If we examine the trend very closely we note some irregularities. The high values for Be and Mg are attributed to the stability of a filled s orbital. The high values for N and P depict that a half-filled p orbital is also stable. The values for B and Al are lower because removal of electron takes place from the singly occupied $2p$ and $3p$ sub-shells respectively. The $2p$ is higher in energy than the $2s$, so the $2p$ electron of B is more easily removed than a $2s$ electron of Be. Similarly the $3p$ electron of Al is more easily removed than $3s$ electron of Mg.

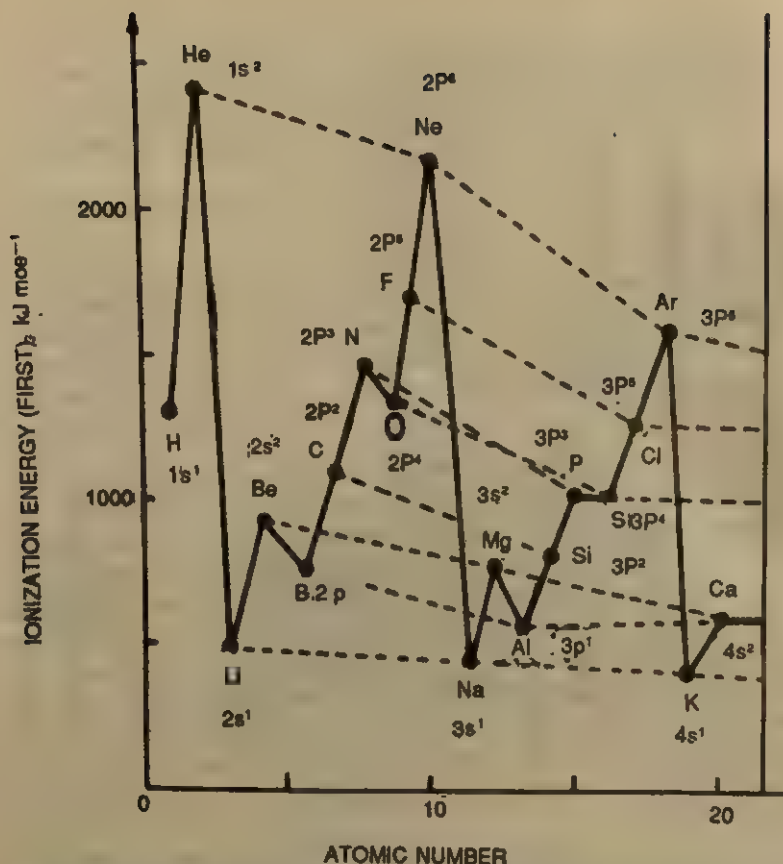


Fig.5.21 The variation of 1st ionization energy with atomic number across the 1st, 2nd and 3rd periods including K and Ca. The orbital of the electron removed is shown for each element

Nitrogen has a $2s^2 2p^3$ configuration in which the three p orbitals are occupied by one electron each. Since the next electron must enter one of these three orbitals, it will experience considerable electron - electron repulsion and will, therefore, be less stable and easier to remove from the oxygen atom. In the third period both phosphorus and sulphur show a similar effect.

The first ionization energy values of noble gases are the highest in their periods (Figs. 5.20 and 5.21) because it requires a great deal of energy to break a stable filled shell of electrons. In general, the first ionization energy decreases in a regular way on descending the main groups (Fig.5.22). A departure from this trend occurs in group 13 owing to the

insertation of the transition elements between the elements of groups 2 and 13. The insertion of d electrons have a bearing effect on the values for Ga, In and Tl. The trend in the transition series is irregular. The additional electrons in these elements occupy the inner (n-1)d level but the electron to be ionized, *i.e.*, *ns* is in the higher level. In successive elements, the increased nuclear charge is largely shielded by the additional (n-1)d electrons and the higher level *ns* electrons experience almost the same effective nuclear charge. As a result, ionization energies remain almost constant across a row of transition metals (Fig. 5.23). Table 5.14 gives 1st ionization energy for various elements.

Figure 5.20 also shows the periodicity for the first ionization energy with atomic number across each period. For example, (i) noble gases with the highest ionization energies in each period occupy the maximal positions, and thus, confirm their stable configurations, and (ii) alkali metals with the lowest values of ionizations energy occupy the minimal positions, and thus, confirm their highly reactive nature.

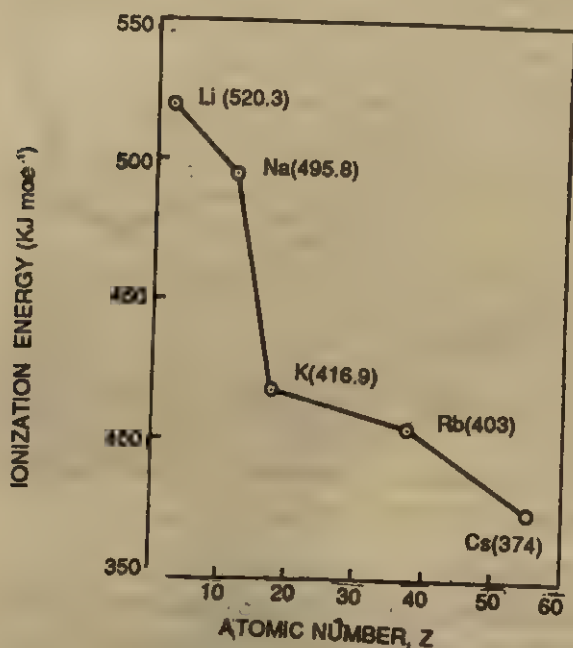


Fig. 5.22 The variation of first ionization energy with atomic number for alkali metals

TABLE 5.14 1st ionization energies for the elements (kJ mol^{-1})

H							He
1312							2372
Li	Be	B	C	N	O	F	Ne
520	899	801	1086	1402	1314	1681	2080
Na	Mg	Al	Si	P	S	Cl	Ar
496	738	578	787	1012	100	1251	1520
K	Ca	Ga	Ge	As	Se	Br	Kr
418	594	586	770	954	946	1150	1360
Rb	Sr	In	Sn	Sb	Te	I	Xe
403	556	565	715	841	879	1020	1180
Cs	Ba	Tl	Pb	Bi			Rn
374	510	594	724	711			1040

First transition metal series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
633	658	650	652	717	762	758	736	745	906

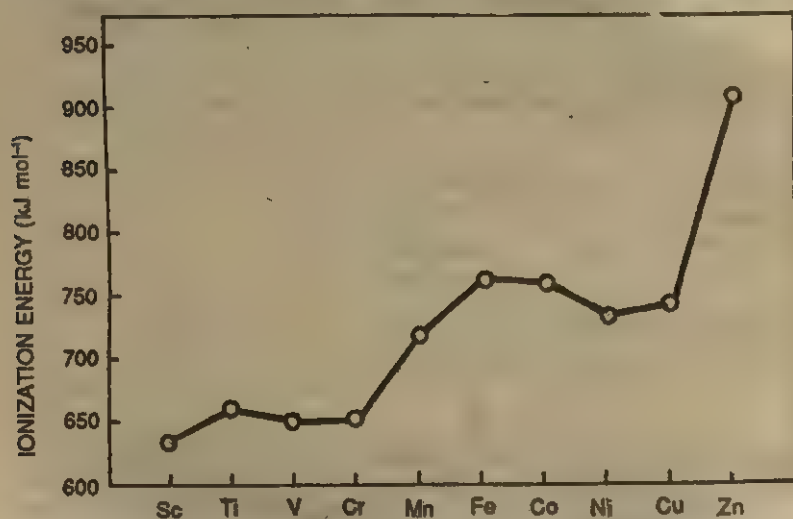
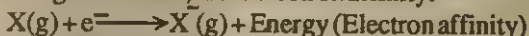


Fig. 5.23 The variation of first ionization energy with atomic number across the first series of transition metals.

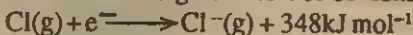
5.7.5 Electron Affinity

It is believed that charge of an electron in an atom is located in a very small volume; in principle the charge cloud extends to infinity. As a result, the positive charge of the nucleus is never fully balanced by the orbiting electrons. This makes atoms to attract to themselves. If any orbital is empty to accommodate an electron within the atom, energy is released.

The energy change, when an electron is added to an isolated gaseous atom in its ground state, is the electron affinity.



For example, the electron affinity of the Cl atom is 348 kJ mol^{-1} . Thus, 348 kJ energy is released when 1 mole of Cl atoms combines with 1 mole of electrons to give 1 mole of Cl^- ions.



The greater the electron affinity of an element, the more stable is its anion with a -1 charge. Positive values of electron affinity, by convention, show the release of energy (exothermic) in anion formation. For a few elements energy is required to add an electron (endothermic), so the electron affinity is negative (Fig. 5.24).

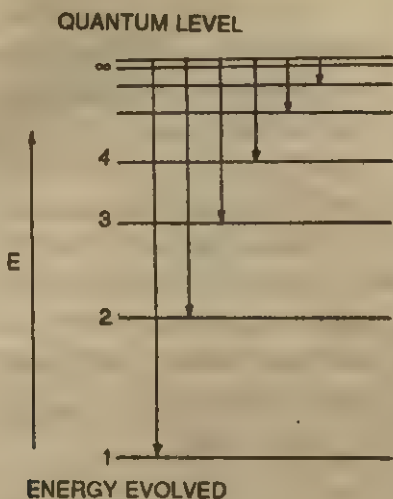


Fig. 5.24 Energy level diagram for the addition of electrons. The energy evolved depends on the level to which the electron falls

There are cases, when more than one electron are added to the outershell of the atom. For example, oxygen can form an ion, O^{2-} . Having acquired an electron, an atom becomes negatively charged, and therefore, addition of second electron requires supply of energy. Thus, the electron affinities subsequent to the first are endothermic quantity. Table 5.15 contains electron affinities of some elements.

The periodic variation in electron affinity generally parallels the variation in atomic size as it involves the placement of an electron into the outershell of the atom. In Table 5.15, we observe that electron affinity generally increases as we move from left to right across a period (Fig. 5.25) as atoms become smaller and the nuclear charge increases. As we

move down a group, electron affinity generally decreases with increasing atomic size (Fig. 5.26). Attraction of the electron is always affected by the nuclear charge and shielding effect. The closer the electron can get to the nucleus, the greater the effect of the nuclear charge. Therefore, small atoms (elements from groups 16 and 17) have very large electron affinities

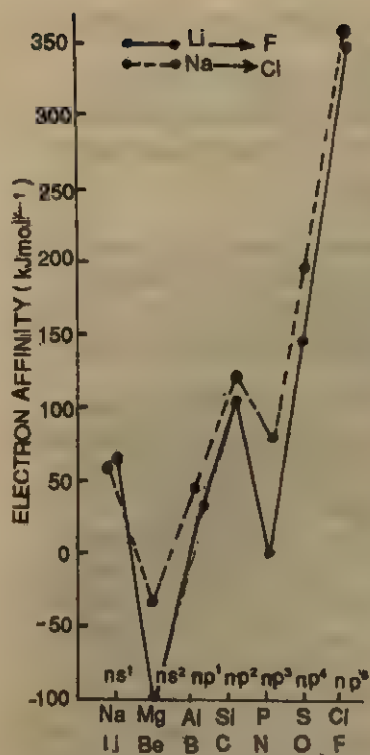


Fig 5.25 Variation in electron affinities for the second and third period elements. Orbital to which electron is added is also shown

because outershells are not screened, and thus, experience a high effective nuclear charge. This causes a strong affinity between the nuclear charge and the outer electrons. On the other hand, large atoms (*e.g.*, elements from groups 1 and 2) have small electron affinities because their outershells feel the effect of a small effective nuclear charge.

From Table 5.15, we find that the non-metals, *e.g.*, N, O and F have lower electron affinities than the elements just below them, *e.g.*, P, S and Cl (Fig. 5.25). This is a matter of surprise because in a given group, size increases on going down. Apparently, the incoming electron experiences repulsion from the electrons already present within the small atomic volume, which leads to a lesser value for electron affinity.

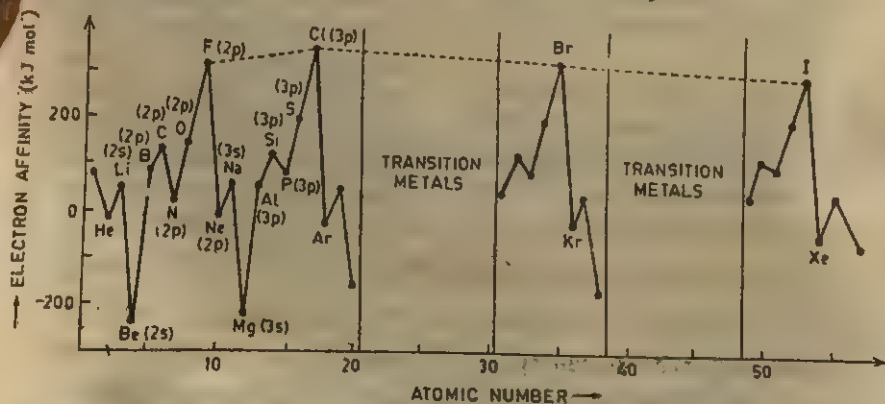


Fig. 5.26 (a) Periodicity in electron affinities of the representative elements, and (b) Variation in electron affinities for the halogen family.

The electron affinities can be correlated with electron configurations. The addition of electron for group 1 elements is somewhat exothermic, even though these elements have low attraction for their single

TABLE 5.15 Electron affinities for some elements (kJ mol^{-1})

H							He
73							-21.23
Li	Be	B	C	N	O	F	Ne
60	-100	27	122	-9	141	333	-28.95
Na	Mg	Al	Si	O	S	Cl	Ar
53	-30	44	134	72	200	348	-34.73
K	Ca	Ga	Ge	As	Se	Br	Kr
48		30	120	77	195	329	-38.59
Rb	Sr	In	Sn	Sb	Te	I	Xe
47		30	121	101	190	295	-40.52
Cs	Ba	Tl	Pb	Bi			Rn
45		30	110	110			-40.52

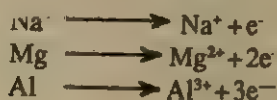
electron, because the incoming electron occupies the lowest sub-level, an ns orbital. In each period, for group 2 elements, like Be and Mg, the addition of electron is endothermic because the electron is added to a higher energy np orbital. The increased nuclear charge from groups 1 to 13 and 14 makes the addition of electron easier, hence, the process is exothermic.

In case of group 15 elements, the incoming electron enters a half-filled p orbital and becomes paired. This process is not energetically favourable, especially in the case of nitrogen.

The experimental determination of electron affinity is difficult. Values have been determined by mass spectrometry for a few elements and in some other cases have been assigned indirectly from thermodynamic data. Thus, it is difficult to draw generalizations from the limited data available, but it appears that electron affinities tend to increase across a period as the atomic number increases. Trends within groups are not clear.

5.7.6 Metallic and Non-Metallic Nature of the Elements

Metals tend to form positive ions and non-metals tend to form negative ions. From this point of view, metallicity and non-metallicity are entirely relative and are related to electronic structures. If you recall, you will remember that Na, Mg and Al can be converted to positively charged ions, e.g.,



Such elements are called electropositive elements. Now if you refer to the periodic table, you will see that in going from left to right within a period, each successive element has one additional electron added to the same shell and one additional proton added to the nucleus. The result is an increase in electron density. The corresponding nuclear charge exerts a greater attraction for the electrons. As a result, valence electrons are pulled more effectively by the nucleus.

Now on comparing the elements from the same period, say sodium and magnesium, it is concluded that valence electron in sodium is less tightly bound than in magnesium. It is, therefore, easier to remove an electron from sodium than from magnesium. On the basis of a similar argument, the elements belonging to the period 3 will lose an electron in the following order : $\text{Na} > \text{Mg} > \text{Al} > \text{Si} > \text{P} > \text{S} > \text{Cl}$. In other words, the electropositive or metallic character decreases from $\text{Na} \longrightarrow \text{Mg} \longrightarrow \text{Al} \longrightarrow \text{Si} \longrightarrow \text{P} \longrightarrow \text{S} \longrightarrow \text{Cl}$.

Elements like F, O, N, etc. acquire electrons and become negatively charged ions. Such elements are called electronegative elements. On the basis of logic used earlier there is an overall decrease in the size of an atom across a period from left to right. In general, as the size decreases the atom becomes more compact and the effect of nuclear charge becomes more pronounced. This results into a corresponding increase in the ability of the atom to attract an electron to itself. Thus, F will have a stronger tendency to acquire electron than O and N. Therefore, fluorine is more electronegative than oxygen and nitrogen. Thus, in a period electronegative or non-metallic character gradually increases from $\text{Li} \longrightarrow \text{Be} \longrightarrow \text{B} \longrightarrow \text{C} \longrightarrow \text{N} \longrightarrow \text{O} \longrightarrow \text{F}$.

Elements show an increase in electropositive character within a periodic group from top to bottom. With each successive element, the added electrons occupy new energy levels. Despite the increased nuclear charge, this causes an increase in distance of the electrons present in the outermost shell from the nucleus. Thus, the addition of a new energy level to an atom dominates over the effect of increase in the nuclear charge. As a result, electrons present at a larger distance can be removed easily as compared to the electrons close to the nucleus. This ease of removal of electrons from an element makes it more electropositive. Thus, for group 1 elements the ease of removal of an electron increases from $\text{Li} \longrightarrow \text{Na} \longrightarrow \text{K} \longrightarrow \text{Rb} \longrightarrow \text{Cs}$, i.e., the electropositive character increases from lithium to caesium. On the basis of this logic one can also explain the transition from non-metallic to metallic nature observed in groups 14, 15, and 16 elements. In group 14, C is a non-metal but Sn and Pb are metals. Similarly in group 15, N is a non-metal whereas Bi is a metal. In group 16, oxygen and sulphur are non-metals whereas Te is a metalloid. Figure 5.5 shows the progressions of all the periodic properties just discussed.

Further support to the trends observed in the case of metallic and non-metallic nature of elements can be arrived at by knowing the nature of oxides (or hydroxides). Trends in the acid-base character of the oxides of s and p-block elements (representative elements) are shown in Fig. 5.27. Electropositive elements form basic oxides (or hydroxides) whereas the electronegative elements form acidic oxides (or acids).

INCREASING ACIDIC CHARACTER →

METALLOIDS

	LI	Be	B	C	N	O	F	
	Na	Mg	Al	Si	P	S	Cl	
	K	Ca	Ga	Ge	As	Se	Br	
	Rb	Sr	In	Sn	Sb	Te	I	
	Cs	Ba	Tl	Pb	Bi			
	BASIC OXIDES			AMPHOTERIC OXIDES		ACIDIC OXIDES (EXCEPT CO, NO, N ₂ O, Fe ₂ O ₃)		

(PARTIAL SHADING EXHIBITS ONE OXIDE AMPHOTERIC WHILE THE OTHER IS BASIC OR ACIDIC)

↑ INCREASING BASIC CHARACTER

METALS

NON-METALS

Fig. 5.27 (i) Acidic and basic properties of the representative elements and
(ii) Classification of the elements as metals, metalloids and, non-metals on the basis of acid-base character of their group oxides

5.7.7 Properties of Hydroxides of Alkali and Alkaline Earth Metals

Hydroxides of alkali and alkaline earth metals are white crystalline solids. Hydroxide stability increases with increasing cation size. Their ionic nature increases with increasing cation size. Thus, ionic character and, hence, alkali strength increases from LiOH to CsOH; and from, Mg(OH)₂ to Ba(OH)₂. The solubility of the hydroxides of alkaline earth metals increases from magnesium to barium : Mg(OH)₂ < Ca(OH)₂ < Ba(OH)₂ (Table 5.16) and is lower than alkali metals. The hydroxides of Be and Mg are insoluble. Beryllium hydroxide is amphoteric in nature, Mg(OH)₂ is a weak alkali, Ca(OH)₂ and Sr(OH)₂ are moderately strong alkalis, and Ba(OH)₂ is nearly as strongly basic as the hydroxides of alkali metals.

Hydroxides of alkaline earth metals are weaker bases than the hydroxides of the alkali metals because of their lower solubility and reduced ionic character.

TABLE 5.16 Solubilities of hydroxides of alkaline earth metals in water at 298 K

Property	Be(OH) ₂	Mg(OH) ₂	Ca(OH) ₂	Sr(OH) ₂	Ba(OH) ₂
Solubility(g/L) in water	Insoluble	0.03	1.3	8	38

5.7.8 Properties of Halides of Alkali and Alkaline Earth Metals

Tables 5.17 and 5.18 include some properties of alkali metals halides.

TABLE 5.17 Properties of chlorides of alkali metals

Property	LiCl	NaCl	KCl	RbCl	CsCl
Colour	White	White	White	White	White
Melting point (K)	883	1081	1045	990	918
Boiling point (K)	1655	1738	1680	1654	1573
Density (g/cm ³)	2.07	2.16	1.99	2.76	3.97
Solubility (g/L)	850	360	350	940	1900

TABLE 5.18 Properties of fluorides of alkali metal

Property	LiF	NaF	KF	RbF	CsF
Melting point (K)	1118	1268	1129	1048	955
Boiling from (K)	1854	1977	1774	1681	1523
Solubility (g/L) in water at 298K	2.7	42.2	1020	1310	3700

Tables 5.19 and 5.20 give some properties of alkaline earth metals halides.

TABLE 5.19 Properties of chlorides of alkaline earth metals

Property	BeCl ₂	MgCl ₂	CaCl ₂	SrCl ₂	BaCl ₂
Colour	White	White	White	White	White
Melting point (K)	678	987	1045	1148	1623
Boiling point (K)	761	1691	1873	1523	—
Density (g/cm ³)	1.899	2.316	2.512	3.052	3.856
Solubility in (g/L) water at 298K	720	550	830	560	370

TABLE 5.20 Properties of fluorides of alkaline earth metals

Property	BeF ₂	MgF ₂	CaF ₂	SrF ₂	BaF ₂
Melting point (K)	795	1536	1691	1673	1593
Boiling point (K)	1073	2500	2773	2733	2533
Solubility (g/L) in water at 298K	Soluble	0.13	0.016	0.72	1.6

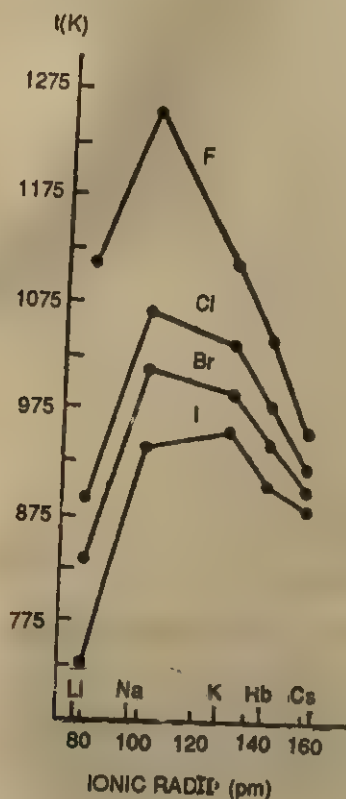


Fig.5.28 Trends in the melting points of alkali metal halides

agrees with the experimental solubilities. However, the reverse solubility order is observed for the iodides, with caesium iodide being the least soluble: $\text{LiI} > \text{NaI} > \text{KI} > \text{RbI} > \text{CsI}$.

On examining the Tables 5.17 and 5.18 and Fig. 5.28, we observe that the melting points of halides of alkali metals decrease in the order: fluoride > chloride > bromide > iodide. Figure 5.28 for the melting points of halides of alkali metals suggest that lithium halides generally melt at lower temperature than those of other alkali metal halides (with one or two exceptions because of the difference in the bonding). Table 5.19 shows that the melting points of alkaline earth chlorides increase from Be to Ba. For their fluorides, melting point increases from beryllium downwards in the group. Solubilities of alkali metal halides in water at 298K have been plotted in Fig. 5.29. Trends in solubility depend upon the nature of lattice. Thus, the order of solubility of the alkali metal fluorides, in which the lattice energy decreases from LiF to CsF should be: $\text{LiF} < \text{NaF} < \text{KF} < \text{RbF} < \text{CsF}$ which agrees

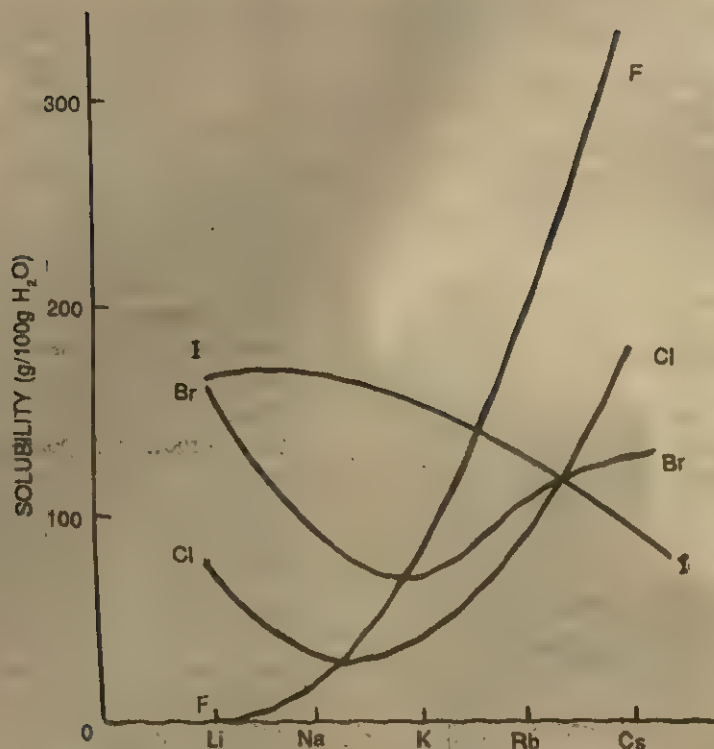


Fig. 5.29 Solubilities of halides of alkali metals at 298 K

5.7.9 Properties of Sulphates and Carbonates of Alkali and Alkaline Earth Metals

The solubility of the sulphates of alkali and alkaline earth metals in water decreases on descending the group. For example, magnesium sulphate is freely soluble but calcium sulphate is only slightly soluble and the sulphates of Sr and Ba are virtually insoluble. Although, essentially all alkali metal compounds dissolve well in water, some common alkaline earth compounds such as MgO , MgF_2 , CaF_2 , SrCO_3 , SrSO_4 and BaSO_4 do not.

The alkali metal carbonates are white solids, soluble in water (except Li_2CO_3) and stable to heat. Carbonates of Na, K, Rb and Cs are deliquescent. Lithium carbonate is insoluble in water and is readily decomposed by heat.

The alkaline earth metal carbonates are white solids, soluble in water and unstable to heat. Unlike the alkali metal carbonates (other than Li_2CO_3), they decompose when heated giving the oxides and CO_2 . The

stability to heat and solubility in water increase from Mg to Ba (according to basic character). Both Be and Mg carbonates are insoluble in water.

The factors influencing the solubility of compounds are out of the scope of this book. The analysis of the solubilities data reveal that trends in solubilities of group 1 and 2 compounds are complex. In fact, almost all group 1 compounds are soluble in water. Sodium and potassium compounds are, for this reason, widely employed as sources of negative ions.

TABLE 5.21 Melting points (K) of halides of alkaline earth metals

Metals	F	Cl	Br	I
Be	795	678	761	783
Mg	1536	987	984	973
Ca	1691	1045	1003	1013
Sr	1673	1148	916	780
Ba	1593	1623 (1236)	1120	984

The trends in solubilities in group 2 compounds are also difficult to generalize. For example, the hydroxides become more soluble down the group, whereas, the reverse is true for sulphates. Trends in solubility of group 2 compounds are given below :

Chlorides	————	All soluble
Carbonates	————	All insoluble
Sulphates	————	Be, Mg soluble; Ca, Sr, Ba insoluble
Hydroxides	————	Be, Mg insoluble; Ca, Sr, Ba soluble.

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

5.1 Put a (✓) mark against the most appropriate choice :

- The law of octaves was advanced by
(a) Newlands (b) Dobereiner (c) Lothar Meyer (d) Mendeleev
- The basis on which Mendeleev constructed his periodic table is :
(a) atomic number (b) atomic mass
(c) atomic volume (d) atomic size
- Which of the following elements did not find place in the Mendeleev's original periodic table?
(a) Aluminium (b) Silicon (c) Zinc (d) Germanium
- Which of the following sets of elements do not belong to the same period of the periodic table?
(a) F, Cl, Br, (b) C, N, O (c) Na, Mg, Al (d) P, S, Cl
- Which of the following sets of elements do not belong to the same group of the periodic table ?
(a) Cu, Ag, Au (b) Li, Na, K (c) Mg, Ca, Sr (d) Al, Si, P
- Which of the following elements is the most electronegative?
(a) Fluorine (b) Chlorine (c) Bromine (d) Iodine

- (vii) Which of the followings describe the process of addition of an electron to an atom?
 (a) Electronic configuration (b) Atomic size (c) Atomic number (d) Valency
- (viii) Which of the following statements concerning atomic size is correct?
 (a) Atomic size increases with increase of atomic number in a period.
 (b) Atomic size increases with increase of atomic number in a group.
 (c) Atomic size is independent of atomic number.
 (d) All of the above.
- (ix) The first ionization potential of Na, Mg, Al, and Si are in the order. (IIT 1988)
 (a) $\text{Na} < \text{Mg} > \text{Al} < \text{Si}$ (b) $\text{Na} > \text{Mg} > \text{Al} > \text{Si}$
 (c) $\text{Na} < \text{Mg} < \text{Al} > \text{Si}$ (d) $\text{Na} > \text{Mg} > \text{Al} < \text{Si}$
- (x) Atomic radii of fluorine and neon in Angstrom unit are respectively given by (IIT 1987)
 (a) 0.72, 1.60 (b) 1.60, 1.60 (c) 0.72, 0.72 (d) None of these values.
- (xi) The first ionization potential in electron volts of nitrogen and oxygen atoms are respectively given by
 (a) 14.6, 13.6 (b) 13.6, 14.6 (c) 13.6, 13.6 (d) 14.6, 14.6
- (xii) Which of the following electronic configurations represent the atom with the largest first ionization potential?
 (a) $[\text{Ne}] 3s^2 3p^2$ (b) $1s^2 2s^2 2p$ (c) $[\text{Ne}] 3s^2 3p^4$ (d) $[\text{Ar}] 3d^{10} 4s^2 4p^3$
- (xiii) A representative element that is a metal is
 (a) Zn (b) Cr (c) Sr (d) Sc
- (xiv) Which of the following salts is not soluble in water?
 (a) BaSO_4 (b) NaCl (c) BaCl_2 (d) Na_2SO_4
- (xv) Which of the following ions has the smallest radius?
 (a) Li^+ (b) Be^{2+} (c) O^{2-} (d) F^-

5.2 Fill in the blanks

- (i) The elements are arranged in the periodic table in order of their increasing
- (ii) The horizontal rows of elements in the periodic table are called
- (iii) The elements in the vertical columns of periodic table constitute
- (iv) The properties of an element are a periodic function of its
- (v) Elements with eight electrons in their outermost energy level are called
- (vi) The elements can be divided into blocks according to their
- (vii) The metallic character with increase of atomic number in a group.
- (viii) From left to right within a period, the strength with which the nucleus attracts the electrons in the outer energy level
- (ix) of fluorine does not fall in line with the general trend.
- (x) A graph of the first ionization potentials of the elements plotted against helps in finding out the number of in a principal energy level.

5.3 Point out the correct statements of the followings:

- (i) The elements, when arranged in order of increasing atomic number, exhibit a periodicity in properties.
- (ii) The size of atoms increases in descending a group in the periodic table.
- (iii) The elements are arranged in the periodic table (long form) in order of their increasing atomic masses.
- (iv) From left to right within a period, the strength with which the nucleus attracts the electrons in the outer energy level increases.
- (v) The elements occupying the centre and left of the periodic table are classified as metals.
- (vi) Mendeleev in his periodic table put argon before potassium even though the atomic mass of argon is higher than that of potassium.
- (vii) Elements having the same atomic masses are called isotopes.
- (viii) Isotopes of elements have been assigned separate place in the long form of periodic table.
- (ix) Magnesium is more electropositive than sodium.
- (x) Elements with 8 electrons in the outer shell are called noble gases.

5.4 Match the descriptions under column B against the statements/terms given under column A.

COLUMN 'A'

COLUMN 'B'

- | | |
|-----------------------------|-------------------------------------------|
| (i) Periods | 1. Belongs to p-block |
| (ii) Groups | 2. Vertical columns of the periodic table |
| (iii) Copper | 3. Belongs to d-block elements |
| (iv) Aluminium | 4. Horizontal rows of the periodic table |
| (v) Alkali metals | 5. Elements belonging to group 1 |
| (vi) Transition elements | 6. Elements from groups 4 to 12 |
| (vii) Sulphur | 7. A unit for expressing energy |
| (viii) kJ mol^{-1} | 8. Avogadro's number |
| (ix) 6.022×10^{23} | 9. A noble gas |
| (x) Neon | 10. A representative element |

Short Answer Questions

- 5.5 (i) Give the terms used to express the following :**
- Vertical columns in a periodic table
 - Horizontal rows in a periodic table
 - Elements having the same atomic number
 - Elements which form both acidic and basic oxides
 - Elements having one electron in the outer shell
 - Elements toward the upper right of the periodic table
- (ii)**
- Using the modern periodic table give the two pairs of elements where the atomic masses are in the opposite order to the atomic numbers.
 - Which has the larger radius ?
(i) Mg or Ca (ii) S or Cl
 - Which is more metallic ?
(i) Na or Mg (ii) C or Si
- (iii)** Choose the alkali metal, noble gas, alkaline earth metal, halogen or transition metal of the following elements :
Sr, K, Xe, Zn, Mn, Fe, He, H, F, I, S and Cl.
- (iv)** What is the fundamental difference between the groups A and B which are used in the Mendeleev periodic table?
- (v)** In terms of electronic configuration, what the elements of a given period and group have in common ?
- (vi)**
- Which two elements of the followings belong to the same period ?
Al, Si, Be and O
 - Which two elements of the followings have structural similarity ?
Na, K, Ne and Ca.
 - Which of the following electronic arrangements represent metals ?
2, 8, 2; 2, 8, 7; 2, 8, 8 and 2, 8, 1.
- (vii)** Among the elements Li, K, Ca, Sr and Kr which one has the lowest first ionization energy? Which one has the highest first ionization energy?
- (viii)** Among the elements Li to Ne, pick out the elements
- With the highest first ionization energy
 - With the highest electronegativity
 - With the largest atomic radius
 - That is the most reactive non-metal
 - That is the most reactive metal
- (ix)** Which of the following pairs of elements would you expect to have lower first ionization energy ? Explain.
(a) Cl or F, (ii) Cl or S, (iii) K or Ar, and (iv) Kr or Xe.
- (x)** Why does the first ionization energy increase as we go from left to right through a given period of the periodic table?

- 5.6 (a) Which of the following pairs of elements would have a higher electron affinity? Comment.
 (i) N or O (ii) F or Cl.
 (b) Account for the fact that the 4th period has eighteen elements not eight elements.
 (c) Give the formula of a species that will be isoelectronic with the following atoms or ions.
 (i) Ne, (ii) Cl^- (iii) Ca^{2+} (iv) Rb^+
 (d) How do atomic sizes vary in a group and in a period? Give reasons for the variations.
 (e) Which of the following pairs would have a larger size? Explain.
 (i) K or K^+ (ii) Br or Br^- (iii) O^{2-} or F^-
 (iv) Li^+ or Na^+ , (v) P or As (vi) Na^+ or Mg^{2+}
 (f) The first ($I E_1$) and the second ($I E_2$) ionization energies (kJ mol^{-1}) of a few elements designated by Roman numerals are shown below :-

	$I E_1$	$I E_2$
I	2372	5251
II	520	7300
III	900	1760
IV	1680	3380

Which of the above elements is likely to be

- (i) a reactive metal,
 (ii) a reactive non-metal,
 (iii) a noble gas, and
 (iv) a metal that forms a stable binary halide of the formula, AX_2 ($\text{X} = \text{halogen}$).

TERMINAL QUESTIONS

- 5.1 (a) Which of the alkali metals has
 (i) the largest atomic radius,
 (ii) the smallest number of electrons per atom, and
 (iii) the smallest positive ion?
 (b) Predict with explanation which ion in each pair is the larger :
 (i) Mg^{2+} or Ca^{2+} (ii) K^+ or Ca^{2+} (iii) Cl^- or K^+ (iv) F^- or Cl^- (v) Na or Na^+ ,
 (vi) Br or Br^-
- 5.2 Describe the early attempts to classify the elements leading to Mendeleev's periodic table.
- 5.3 What was the basis on which Mendeleev constructed his periodic table? What were the essential features of Mendeleev's periodic table?
- 5.4 State the present day version of the periodic table. How does it differ from that of Mendeleev's?
- 5.5 Write notes on the followings :
 (a) Dobereiner's triads (b) Newlands' octaves (c) Lothar Meyer's curves
- 5.6 What significance does the periodic table have with regard to the development of theory about the electronic structure of the atom?
- 5.7 Discuss the trends in atomic sizes of elements in the periodic table.
- 5.8 Name the four blocks of elements in the periodic table. State their characteristics.
- 5.9 (a) Which of the following elements belong to p-block?
 Na, Al, S, Cl, Cu, Mg, C
 (b) Which elements constitute the halogens, the noble gases and the alkaline earth metals?
- 5.10 (a) State the modern periodic law
 (b) Why did Mendeleev leave blank spaces in the periodic table? Explain.
- 5.11 What is the screening effect? How does it relate to effective nuclear charge.
- 5.12 The valence of representative element is either equal to the number of the valence electrons or eight minus this number what is the basis of this rule?

- 5.13 Lanthanides and actinides are placed in separate rows at the bottom of the periodic table. Give reasons for this arrangement.
- 5.14 Explain the following periodic properties
(i) ionization energy, (ii) valence, (iii) electron affinity (iv) metallic character
- 5.15 Describe and account for the general trend of electron affinities across one period using this data below: Also explain the low value for the electron affinity of P.

	Si	P	S	Cl
EA kJ mol ⁻¹	120	74	200	348

ANSWERS TO SELF ASSESSMENT QUESTIONS

- 5.1 (i) (a), (ii) (b), (iii) (d), (iv) (a), (v) (d), (vi) (a), (vii) (a), (viii) (b), (ix) (a), (x) (a), (xi) (a), (xii) (b), (xiii) (c), (xiv) (a), (xv) (b)
- 5.2 (i) atomic number, (ii) periods, (iii) groups, (iv) atomic number, (v) noble gases, (vi) four, electronic configuration, (vii) increases, (viii) increases, (ix) electron affinity (x) atomic number, orbitals
- 5.3 Statements (i), (ii), (iv), (v), (vi) and (x) are correct
- 5.4 (i) 4, (ii) 2, (iii) 3, (iv) 1, (v) 5, (vi) 6, (vii) 10, (viii) 7, (ix) 8, (x) 9.
- 5.5 (i) (a) group, (b) period, (c) isotopes, (d) metalloids, (e) alkali metals, and (f) non-metals
- (ii) (a) Argon and potassium; cobalt and nickel
(b) (i) Ca (ii) S; (c) (i) Na (ii) Si
- (iii)
- | | | |
|----------------------|---|-------------|
| Alkali metal | : | K, |
| Alkaline earth metal | : | Sr, |
| Noble gas | : | Xe, He |
| Transition elements | : | Mn, Zn, Fe, |
| Halogen | : | F, I, |
- (iv) (b) Group A elements are representative elements and group B elements are transition elements
- (v) (a) For elements in a period the number of shells is equal; for elements in a group the number of electrons in the outermost shell is the same
- (vi) (a) Al and Si, (b) Na and K (c) 2, 8, 1 and 2, 8, 8, 2.
- (vii) Lowest ionization energy : K
Highest ionization energy : Kr
- (viii) (i) Ne, (ii) F, (iii) Li, (iv) F (v) Li
- (ix) (i) Cl, because its size is larger than F
(ii) S, because its size is larger than Cl and it has been placed earlier than Cl in the same period
(iii) K, Potassium is an alkali metal with (Ar) 4s¹ while Kr is a noble gas with (Ar) 3d¹⁰ 4s² 4p⁶
(iv) Xe, because its size is larger than Kr
- (x) The first ionization energy increases due to the increased nuclear charge across the period.
- 5.6 (i) Oxygen : Oxygen is more electronegative than nitrogen. The incoming electron in the case of N is added to a half filled p orbital. Hence, the process is endothermic. In the case of oxygen the process is relatively exothermic as the unscreened nuclear charge increases by one unit.
- (ii) Cl ; Apparently it is because the fluorine atom is small and the incoming electron is repelled by the electrons already present within the small atomic volume.
- (b) A graph of the first ionization energies of the elements plotted against atomic number answers this question as it tells us about the number of orbitals that can be possible for principal energy level $n = 4$. It involves extra 3d orbital which can accommodate 10 electrons.

(c) (i) Na^+ or F^- , (ii) Ar or Ca^{2+} (iii) Ar or Cl^- (iv) Kr or Sr^{2+}

(d) For detailed answer see under periodic properties. Increased effective nuclear charge across the period makes the outermost electrons come close to the nucleus, which reduces its atomic size.

In a group, atomic size increases from top to bottom as with every element a new principal energy level is added.

(e) (i) K , : because with the removal of electron the effective nuclear charge in K^+ has increased.

(ii) Br^- ; with the acceptance of additional electron the electron cloud has expanded in the case of Br^- . Moreover, the nuclear charge has become less by one unit.

(iii) O^{2-} ; Both O^{2-} and F^- are isoelectronic but the volume of electron cloud in the case of O^{2-} is more than F^- . Also the nuclear charge for O^{2-} has become less by two units.

(v) As ; because As occupies one extra energy level.

(vi) Na^+ ; Both Na^+ and Mg^{2+} are isoelectronic. Na^+ experiences a lower value of effective nuclear charge.

(f) (a) II, (b) IV, (c) I, (d) III.

Bonding and Molecular Structure

To him who is a discoverer in the field (of science), the products of his imagination appear so necessary and natural that he regards them, and would like to have them regarded by others, not as creations of thought but as given realities.

(ALBERT EINSTEIN)

(1879-1955)

UNIT PREVIEW

- 6.1 Introduction
- 6.2 Chemical bond and Lewis structures
 - 6.2.1 Octet rule
 - 6.2.2 Ionic bond
 - 6.2.3 Covalent bond
 - 6.2.4 Coordinate covalent bond
- 6.3 Shapes of molecules
 - 6.3.1 VSEPR theory
- 6.4 Quantum theory of the covalent bond
 - 6.4.1 The hydrogen molecule
 - 6.4.2 Sigma (σ) and pi (π) bonds and some simple molecules: hydrogen, fluorine, hydrogen fluoride, electronegativity, water, oxygen, ammonia
- 6.5 The concept of hybrid orbitals and geometry of molecules
 - sp^3 hybridization : methane, ethane, ammonia and water
 - sp^2 hybridization : ethene, boron trichloride
 - sp hybridization : ethyne, beryllium fluoride
- 6.6 Ionic bond as an extreme case of polar covalent bond
- 6.7 Ionic character of bonds and polar molecules
 - 6.7.1 Molecular polarity and dipole moment
 - 6.7.2 Percentage ionic character of covalent bond
- 6.8 Bonding in solid state
 - 6.8.1 Ionic solids
 - 6.8.2 Molecular solids
 - 6.8.3 Covalent solids
 - 6.8.4 Metallic solids : metallic bond
- 6.9 The hydrogen bond
- 6.10 Resonance

Self assessment questions

Terminal questions

Answers to self assessment questions

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Define and describe chemical bonding by the atomic orbital method
2. Write electron dot formulae (Lewis structures) for atoms and chemically combined atoms
3. Understand the significance of 'octet rule'.
4. State what is meant by ions
5. Recognize that, as a general rule, elements tend to combine to form compounds in which they have a noble gas structure
6. Explain how ionic and covalent bonds are formed between atoms
7. State the conditions governing the formation of ionic and covalent bonds
8. Explain the formation of a dative or coordinate bond
9. Describe the formation of multiple bonding in simple molecules
10. Differentiate between covalent and ionic compounds
11. Write Lewis structures for the various molecules
12. Define the term electronegativity
13. Predict the geometry of simple molecules and polyatomic molecules
14. Understand the meaning of sigma (σ) and pi (π) bonds
15. Identify the type of orbital hybridization associated with the structures of some molecules
16. Give a definition of polar bond and polar molecule
17. Predict the polarity of molecules on the basis of symmetry and asymmetry of covalent bonds
18. Calculate the percentage ionic character of covalent bonds from dipole moment data
19. Demonstrate the relationship between electronegativity and percent of ionic character
20. Explain the bonding in solid state
21. Describe the characteristics of ionic solids, molecular solids, covalent solids and metallic solids
22. Explain and understand the bonding involved in metals
23. Describe hydrogen bond
24. Differentiate between hydrogen bond and other weak forces
25. Understand the meaning of the term resonance

6.1 INTRODUCTION

In Unit 1 we introduced elements, the fundamental substances whose atoms make the basic materials used in constructing all living and non-living things. But the fact is that the isolated atoms of nearly all the elements tend to join strongly together. Although there are only about 107 kinds of basic building blocks, an enormous number of substances have been possible through various types of chemical combinations of atoms. This possibility is fully realized in nature. And with this diversity of substances, is associated the diversity of physical and chemical characteristics shown by nature's most fascinating creations; the tanginess of salt, the transparency of diamond, the fragrance of rose, *etc.*.

Our curiosity is aroused. If the familiar yet somehow mysterious and fascinating characteristics of many substances result from the different arrangements in which nature joins its building blocks, what is mortar that keeps the atoms together? Now, having gained some understanding of the building blocks, we are in a position to know about the mortar. In this unit, we will discuss about chemical bonds and how they are formed.

Why do atoms unite together to form molecules? How are atoms held together; as they are, *e.g.*, in compounds such as NaCl and H_2O and in the molecules of some elements such as H_2 and Cl_2 ? How is bonding achieved?

Following the discovery of the electron and the development of theories of atomic structure, it was suggested that the electrons revolving round the nucleus were involved in the formation of chemical bonds between the atoms. Because the electrons in the completed innershells of an atom are held much more strongly than the electrons in outershells, the innershell electrons are not generally involved when atoms unite. In discussing chemical bonds, we will, therefore, be concerned only with the valence shell electrons. For many years scientists worked in quest of solutions of these and many other such questions. In seeking the solutions they were always conscious of the fact that only a system with minimum energy could be stable. Molecules must obviously be formed with evolution of energy. Hence, they are more stable than atoms.

The first clue to the chemical combination came only from the structure of noble gases and their remarkable inability to enter into chemical combination. It is fair to assume that noble gases have a stable electronic configuration and that the unreactive nature of these elements is due to their special electronic configuration. In 1916, Walter Kossel and Gilbert N. Lewis independently advanced the view that

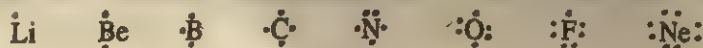
atoms tend to react together so as to attain the stable electronic configurations of the nearest noble gases. In the process of combining, atoms attain either the stable electronic configuration of helium or the configuration of some other gas. Since the atoms of noble gases, with the exception of helium, have eight electrons in their outermost shell, the Kossel and Lewis theory became known as the 'octet rule'. There are many exceptions to the octet rule, but it is still a very useful concept for understanding the chemical bond.

When two similar or dissimilar atoms approach each other, both attractive and repulsive forces start acting on them. As a consequence of these forces, the electrons present in the outermost shells of the atoms rearrange themselves to attain the stable structure of the nearest noble gas. As a result, a molecule is formed if the forces of attraction are stronger than the forces of repulsion. Thus, whenever atoms are held together by strong forces of attraction we say that there is a **chemical bond**. Now we are in a position to say that a chemical bond holds the two hydrogen atoms together in a molecule of hydrogen, H_2 . We would also like to know why molecules like H_3 , H_4 , H_5 , etc., do not exist. Molecules have a definite and distinct shapes. For example, water (H_2O) molecule is V-shaped, methane (CH_4) is tetrahedral, ammonia (NH_3) is pyramidal and so on. The shapes of molecules have a strong bearing on physical and chemical properties. Had, water been a linear molecule instead of being a V-shaped one, it would have had mysterious properties different from those we are used to. Obviously, it is pertinent to study about the factors that are responsible for the distinct shapes and geometries of molecules.

6.2 CHEMICAL BONDS AND LEWIS STRUCTURES

Chemical bonds, as we understand, are strong forces of attraction between atoms. A group of atoms held together by chemical bonds has altogether different properties from the isolated atoms. The attractive forces responsible for molecule formation are the electrical forces between negatively charged electrons and positively charged nuclei. Since valence electrons are usually the only electrons used in the formation of chemical bonds, it is customary to exhibit only the valence electrons in electron dot structures introduced by Lewis. Electron dot structures show valence electrons as dot; the inner electrons and the atomic nuclei are depicted by the symbol for the element being considered. At times electron dot structures are also called Lewis dot structures in honour of Gilbert N Lewis whose idea "that the chemical bond is associated with the electrons in atoms" is very much a part of modern chemistry. Some examples of Lewis dot structures

are



As we discussed in Unit 5, the number of valence electrons of an element corresponds to the group number (or group number -10) of the element in the periodic table. So, the number of electron dots indicates the number of valence electrons. For Li, Be, B and C, this number represents the common valence. Thus, Li and its neighbours in the same group are monovalent. Beryllium and the other alkaline earth metals with two valence electrons show bivalency. Boron (also Al, Ga, *etc.*) is trivalent and carbon is tetravalent (also Si, Ge, *etc.*). However, for elements like nitrogen, oxygen, fluorine and neon the valence is calculated by subtracting the number of electron dots from 8. Thus, nitrogen, oxygen and fluorine have valency, 3, 2 and 1, respectively.

6.2.1 Octet Rule

As already discussed, that one of the first clues regarding chemical bonding came from the noble gas atoms. There are no naturally occurring compounds of these noble gases. They exist in a monoatomic state rather than combining together to form diatomic molecules as other gaseous elements do, *e.g.*, O_2 , N_2 , F_2 , *etc.* Although it is now known that these gases do form molecules. Their little tendency to form chemical compounds predicts that these atoms must be highly stable. What accounts for their unique behaviour? The noble gases are unique in having an electron configuration with an outermost shell of eight electrons. Keeping in view the stability of these gases, Lewis and Kossel (1916) proposed the octet rule. The octet theory states that in a chemical bond formation, atoms either tend to transfer one or more electrons from one atom to another (ionic) or tend to share electrons mutually between atoms (covalent) to achieve the stable electron configuration of 8 electrons in the outermost shell ($ns^2 np^6$). Generally this happens through the formation of one or the other type of bond - ionic (or electrovalent), covalent or coordinate.

6.2.2 The Ionic (or Electrovalent) Bond

Ionic bond results from the force of attraction between oppositely charged ions. Ions are formed when electrons are transferred from one atom to another. As a result, ions acquire stable electronic configuration similar to those of the nearest noble gas. Let us consider this process in more detail by examining the nature of ionic bond in sodium chloride, a typical ionic compound. The electronic configuration of sodium is 2, 8, 1. Only the last electron is important for bonding. If the sodium atom transfers its single valence electron to another atom, it acquires a positive charge (the resulting species has 10 electrons but still 11 protons, hence, it acquires the positive charge carried by the 11th proton). This positively charged species is called a cation (Fig. 6.1).

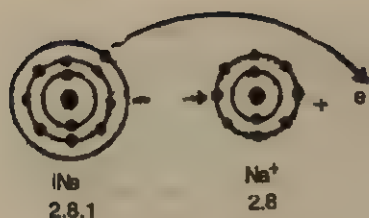


Fig.6.1 Formation of sodium ion. (Neon configuration with 8 electrons in outer shell)

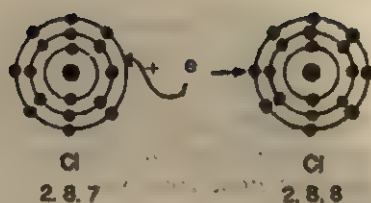


Fig. 6.2 Formation of chloride ion. (Argon configuration with 8 electrons in outer shell)

The electronic configuration of chlorine is 2,8,7. The last seven electrons are valence electrons. If the chlorine atom accepts one electron from the other combining atom, it acquires the negative charge (the resulting species has 18 electrons but still 17 protons, hence, it acquires negative charge due to extra electron). This negatively charged species is called an anion (Fig.6.2).

When sodium chloride forms, the sodium atoms lose electrons (forming sodium ions), transferring them to the chlorine atoms which, in turn, accept them forming chloride ions (Fig. 6.3).

As the sodium atom transfers its valence electron, it attains the electronic configuration of the neon atom (2, 8). As the chlorine atom accepts the electron, it attains the electronic configuration of the argon atom (2, 8, 8). The interaction between a sodium atom and a chlorine atom may be illustrated by electron dot representation (Lewis structure). Figure 6.4 illustrates the Lewis representation.

NOTE : Electrons shown by dots and small circles are identicals. They have been shown by different symbols just to indicate that they belong to different elements.

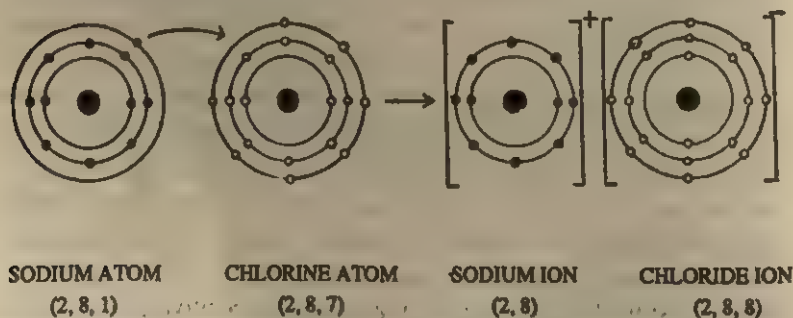


Fig. 6.3 Electrovalent interaction of sodium and chlorine to form sodium chloride

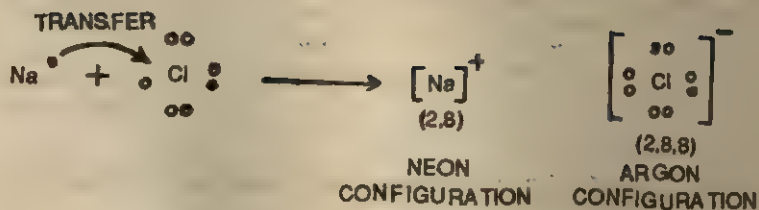
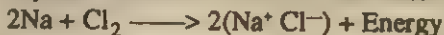


Fig. 6.4 Lewis representation of sodium chloride

The cations and anions that are formed attract each other (by virtue of their opposite charges) to produce an infinite three dimensional crystalline lattice of sodium chloride.



Let us consider a few more examples.

Magnesium Chloride : Magnesium atom has two electrons in its outermost shell. The two electrons are transferred to two chlorine atoms. In this process, magnesium ion (Mg^{2+}) and the two chloride ions (Cl^-) acquire the stable electronic configuration of noble gases. The interaction has been portrayed in Fig. 6.5. Lewis representation of magnesium chloride is given in Fig. 6.6.

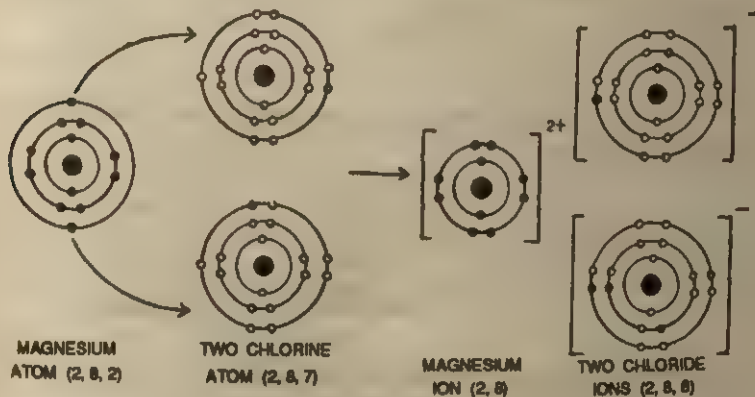


Fig. 6.5 Electrovalent interaction of magnesium and chlorine to form magnesium chloride

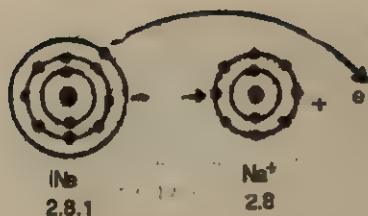


Fig.6.1 Formation of sodium ion. (Neon configuration with 8 electrons in outershell)

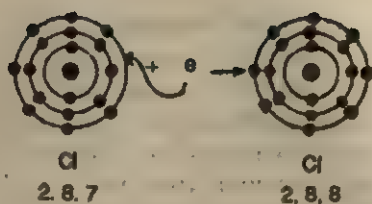


Fig. 6.2 Formation of chloride ion. (Argon configuration with 8 electrons in outer shell)

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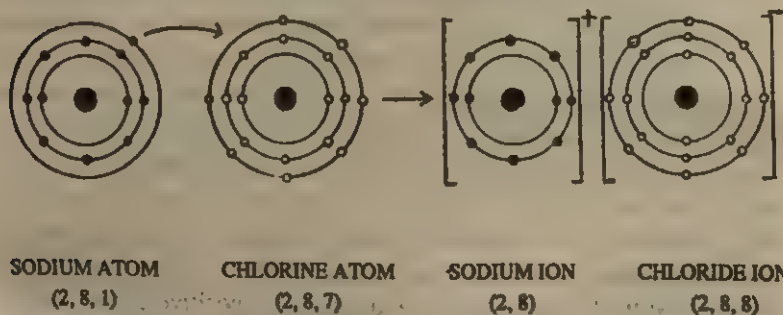


Fig. 6.3 Electrovalent interaction of sodium and chlorine to form sodium chloride

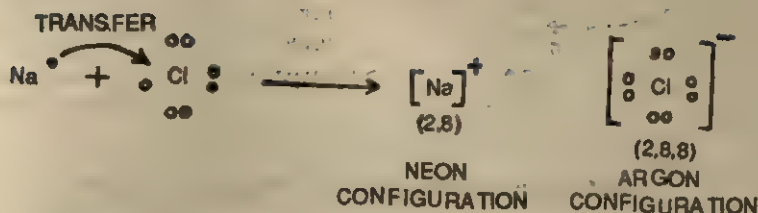
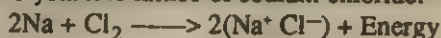


Fig. 6.4 Lewis representation of sodium chloride

The cations and anions that are formed attract each other (by virtue of their opposite charges) to produce an infinite three dimensional crystalline lattice of sodium chloride.



Let us consider a few more examples.

Magnesium Chloride : Magnesium atom has two electrons in its outermost shell. The two electrons are transferred to two chlorine atoms. In this process, magnesium ion (Mg^{2+}) and the two chloride ions (Cl^-) acquire the stable electronic configuration of noble gases. The interaction has been portrayed in Fig. 6.5. Lewis representation of magnesium chloride is given in Fig. 6.6.

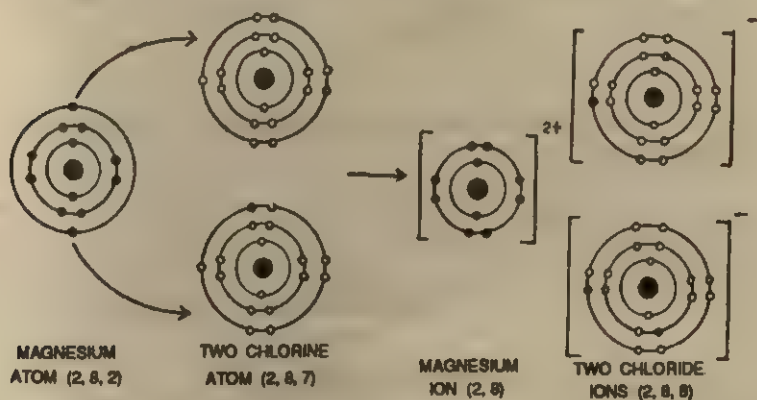


Fig. 6.5 Electrovalent interaction of magnesium and chlorine to form magnesium chloride

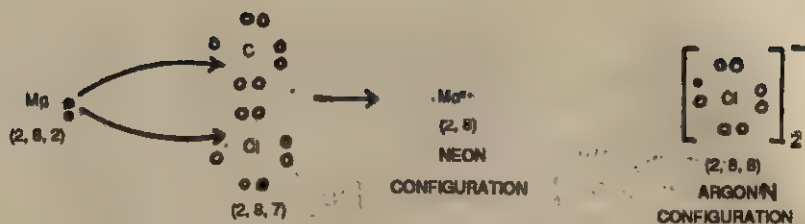


Fig. 6.6 Lewis representation of magnesium chloride

Calcium Oxide : Calcium atom with electronic configuration 2, 8, 8, 2 loses two electrons to form Ca^{2+} ion (2, 8, 8). The two electrons lost by calcium are accepted by oxygen and, in turn, becomes oxide ion, O^{2-} (2, 8). Thus, the atoms attain stable electronic configurations. The diagram for the formation of calcium oxide is shown in Fig. 6.7.

The electron dot representation for calcium oxide is given in Fig. 6.8.

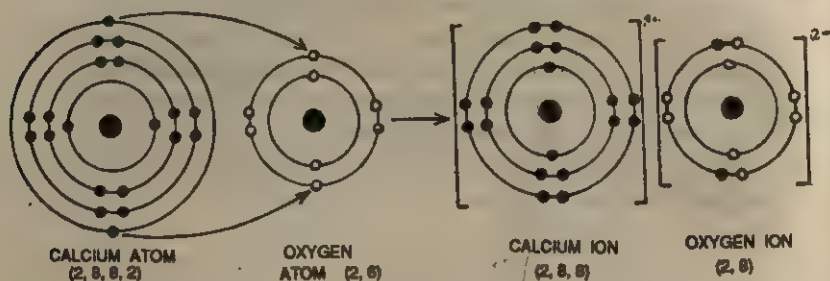


Fig. 6.7 Electrovalent combination of calcium and oxygen to form calcium oxide

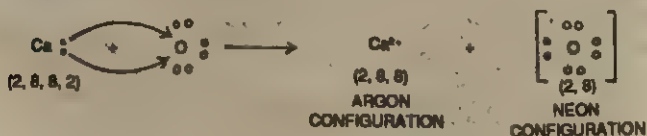


Fig. 6.8 Lewis representation of calcium oxide

The transference and acceptance of electrons in the formation of a few other electrovalent compounds is illustrated in Figs. 6.9 and 6.10.

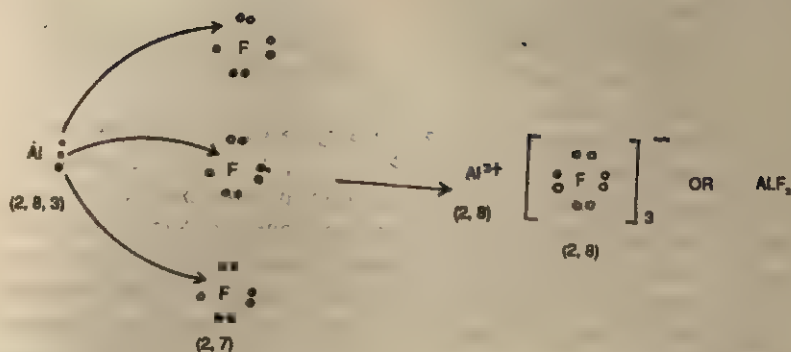


Fig. 6.9 Formation of aluminium fluoride

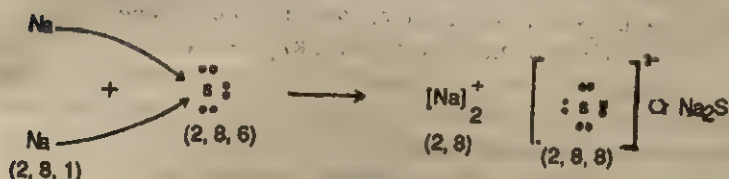


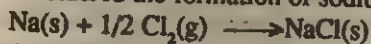
Fig. 6.10 Formation of sodium sulphide

Thus, the number of electrons gained or lost by an atom of an element during chemical combination so as to attain stable configuration is called its *electrovalency*.

From the above it is evident that electronic configuration of an element helps to decide about the nature of elements which can form electrovalent bonds. Generally the element which can donate electrons easily, *i.e.*, electropositive (metallic) elements like, Li, Na, K, Be, Mg, Ca, etc. and the elements which can accept the electrons easily, *i.e.*, electronegative (non-metallic) elements like, F, Cl, O, S, etc. form ionic bonds, and hence, ionic solids.

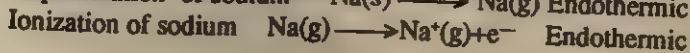
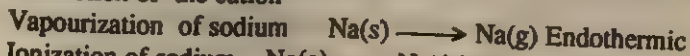
Energy Changes in Ionic Compound Formation

A simple picture of the energy changes involved in the formation of an ionic compound was suggested by M. Born and F. Haber. They considered the formation of sodium chloride from its elements.



According to them it involves three steps as given below :

1. Production of the cation



2. **Production of the anion**
 Dissociation of chlorine $\frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$ Endothermic
 Ionization of chlorine $\text{Cl}(\text{g}) + e^- \rightarrow \text{Cl}^-(\text{g})$ Exothermic
 (electron affinity)
3. **Combinaion of ions to form a crystalline solid** $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{Na}^+\text{Cl}^-(\text{s})$ Exothermic

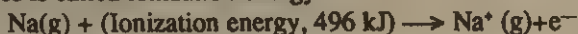
The driving force in the formation of an ionic bond is a lowering of the energy of the particles that come together to form the compound. Thus, in the formation of sodium chloride, solid sodium and chlorine molecules should pass to a lower energy level by forming ionic bonds. In fact, lowering of the energy of a system contributes to its stability.

The process of formation of ionic compounds involves three following steps for which energy data are available. These steps can be illustrated by taking the example of sodium chloride.

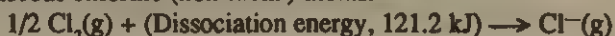
1. **Production of the cation** : It involves the formation of the individual gaseous sodium (metal) atoms from the solid sodium.



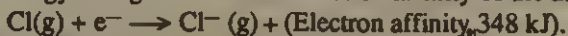
To produce cation, an electron is removed from the neutral gaseous atom. This process takes energy. This energy required in the process is called ionization energy.



2. **Production of the anion** : It involves the formation of individual gaseous chlorine (non-metal) atoms.



To produce anion, an electron is added to the neutral chlorine atom. This process releases energy, i.e., it is a favourable process. This energy change is called the electron affinity of the atom.



Thus, the amount of energy required to produce isolated cation and anion is 378.0 kJ.

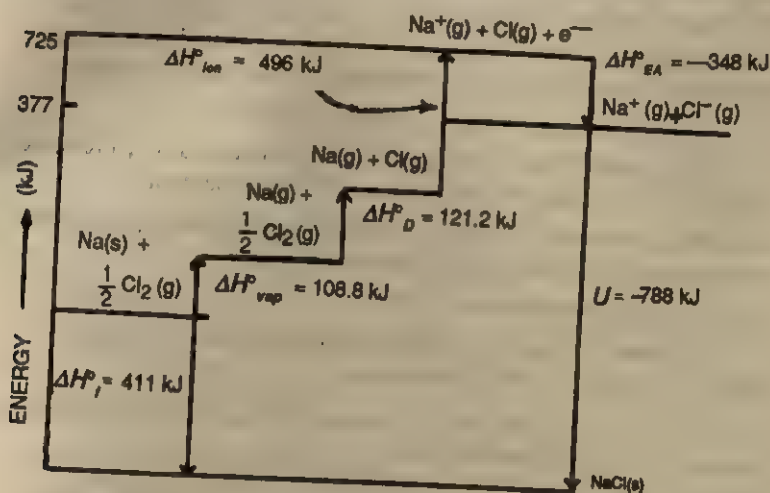
3. **Attraction of oppositely charged ions** : The electron transfer from Na to Cl atom is not favoured energetically. However, $\text{Na}^+ \cdot \text{Cl}^-$ ion pair is formed. The interaction of pair of ions follows a potential energy curve whose form is similar to that in Fig. 6.32

When the isolated charged ions approach to form a crystal, a considerable amount of energy (known as crystal or lattice energy) is released. The magnitude of crystal energy is such that it fulfils the requirement for the first and second steps also. An excess energy is liberated as heat of formation of sodium chloride. Thus, the electrostatic attraction between oppositely charged ions and the formation of the ionic crystal is an integral part of the total process of the ionic bonding. Elements will not produce an ionic compound if it is at a higher

energy level than the elements. They may combine by the formation of covalent bonds.

Solid sodium chloride can be formulated as NaCl or Na^+Cl^- . It represents only the empirical formula. No molecular formula can be assigned as a solid ionic compound does not contain any molecule. With the valence of the elements, empirical formula of an ionic compound can be easily suggested. The valence is equal to the number of charge units on the ion.

From the above it is derived that most stable ionic compounds will result when elements of low ionization energy combine with elements of high electron affinity, or when the lattice energy of the resulting compound is very large or both.



Relative energies of various combinations of sodium and chlorine per mole of each atom.

Since metals generally have low ionization energies and electron affinities, they tend to lose electrons to form cations; non-metals, on the other hand, have large ionization energies and electron affinities, so they accept electrons to give anions. Accordingly most of the compounds obtained from metals and non-metals are ionic, i.e., compounds formed with elements from group 1 and 2 and 7 are ionic.

Electronic structures of the atoms and monoatomic ions of the elements in period 3 are given below.

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Electron structure of the atom	2, 8,	2, 8, 2	2, 8, 3	2, 8, 4	2, 8, 5	2, 8, 6	2, 8, 7	2, 8, 8
Valence electrons	1	2	3	4	5	6	7	8
Ion formed	Na ⁺	Mg ²⁺	Al ³⁺			S ²⁻	Cl ⁻	
Electron structure of the ion	2, 8	2, 8	2, 8	-	-	2, 8, 8	2, 8, 8	
Electron structure of the outer core	s ² p ⁶	s ² p ⁶	s ² p ⁶			s ² , p ⁶	s ² , p ⁶	

Properties of Electrovalent Compounds

1. They contain oppositely charged ions only and have no molecule in them.
2. Their ions are held together by strong electrostatic forces of attraction. Hence, these compounds are solids. Thus, the crystalline solids are a network of ions held together by electrostatic attraction.
3. They have high melting and boiling points.
4. They conduct electricity in the molten state and are, therefore, electrolytes. This is due to the presence of ions in the melt.
5. They are mostly soluble in water, but do not dissolve in organic solvents such as benzene, ether and acetone.
6. They ionize in solution.
7. Aqueous solutions of ionic compounds conduct electricity because ions are present in such solutions.

Exercise 6.1 : Give the valence electron configuration (or electron configuration) of the following ions :

(i) Mn²⁺ (ii) Cu⁺ (iii) Cr³⁺ (iv) Ca²⁺ (v) K⁺ (vi) Cl⁻

Solution : (i) Mn (3d⁵ 4s²) has lost the 4s electrons, so Mn²⁺ has 3d⁵.

(ii) Cu (3d¹⁰ 4s¹) has lost the 4s electron to form Cu⁺ with 3d¹⁰ electron configuration.

(iii) Cr (3d⁵ 4s¹) has lost three electrons to form Cr³⁺, so the ion has 3d³ configuration.

(iv) Ca (4s²) has lost two 4s electrons to give Ca²⁺, so the electron configuration of the outermost shell will be 3s² 3p⁶.

(v) K (4s¹) has lost one electron to give K⁺, so the electron configuration of the outermost shell will be 3s², 3p⁶.

(vi) Cl (3s² 3p⁵) has gained one electron to become Cl⁻, so the electron configuration of the outermost shell will be 3s² 3p⁶

Exercise 6.2 : Predict the formula of the compound formed between the pairs of the elements given below :

(i) Mg, Br (ii) Al, F, (iii) K, O (iv) Na, S, and (v) Li, N

Solution:

Ions formed on the basis
of their position in
periodic table

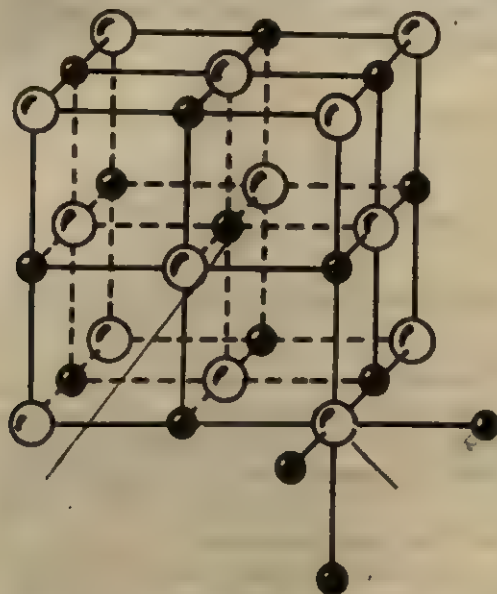
Formula of the compound
on balancing the charges

Lewis structure

Mg^{2+} , Br^{-}	Mg Br_2	(Mg^{2+})	$(\ddot{Br})_2^{-}$
Al^{3+} , F^{-}	AlF_3	(Al^{3+})	$(\ddot{F})_3^{-}$
K^{+} , O^{2-}	K_2O	$(K^{+})_2$	$(\ddot{O})^{2-}$
Na^{+} , S^{2-}	Na_2S	$(Na^{+})_2$	$(\ddot{S})^{2-}$
Li^{+} , N^{3-}	Li_3N	$(Li^{+})_3$	$(\ddot{N})^{3-}$

Structure of Ionic Compounds

Most ionic compounds are crystalline solids at room temperature. Crystals contain samples of matter in which the component molecules, atoms or ions are arranged in repeating three dimensional pat-



terns, *e.g.*, sodium chloride lattice (Fig. 6.11). Each sodium ion (Na^{+}) is surrounded by 6 chloride ions (Cl^{-}) and each chloride ion is surrounded by six sodium ions. Thus, both Na^{+} and Cl^{-} ions have identical environments but are different for the two ions. As a whole, each sodium chloride crystal (big or small) is electrically neutral.

Fig. 6.11 Extended ionic crystal structure of $NaCl$

6.2.3 The Covalent Bond

The covalent bond is formed by the mutual sharing of equal number of valence electrons by the two reacting atoms. The shared or bonded electron pair is associated with both atoms. One or more pair of electrons are held in common by the combined atoms. By sharing electrons, the atoms achieve the chemical stability associated with a

noble gas. Let us consider the formation of fluorine molecule. When two atoms of fluorine unite to form a molecule, one electron is provided by each of the two fluorine atoms; fluorine molecule is formed in which both the fluorine atoms attain the stable octet electronic configuration as shown in Fig. 6.12

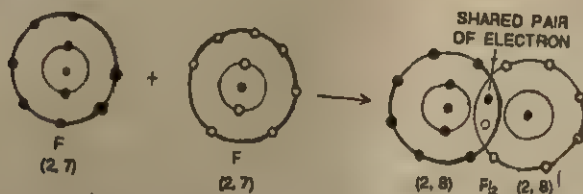


Fig. 6.12 Covalent combination of two fluorine atoms

The combination of two fluorine atoms may be illustrated below by electron dot representation (Fig. 6.13).

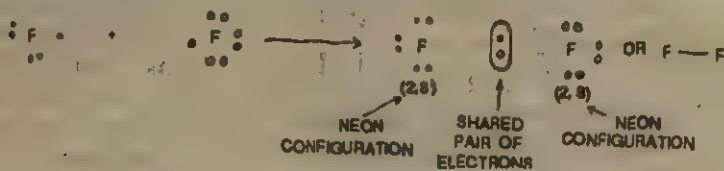


Fig. 6.13 Covalent bond formation in a fluorine molecule - a Lewis representation

The shared pair of electrons constitute the covalent bond. The fluorine molecule with one shared electron pair (represented by a single line, —) will have a single bond. The remaining six pair of electrons that are not mutually shared are called non-bonding electrons.

Hydrogen Molecule : Hydrogen atom contains one electron in its valence shell. In order to form H_2 molecule, both atoms share one electron each so as to create one shared pair of electrons. In the process, both the atoms attain the stable electronic configuration of helium (a duplet of electrons), see Fig. 6.14.

Hydrogen Chloride : When one atom of hydrogen unites with one atom of chlorine, hydrogen attains a duplet of electrons and chlorine attains an octet of electrons by sharing a electron pair, one electron being given by each participants (Fig. 6.15). Figure also includes the Lewis representation of HCl.

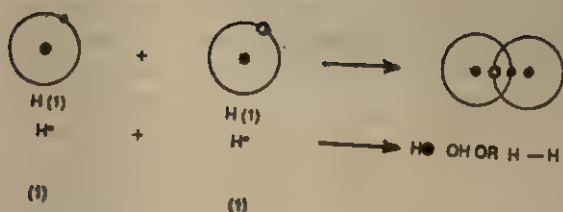


Fig. 6.14 Covalent bonding in a hydrogen molecule

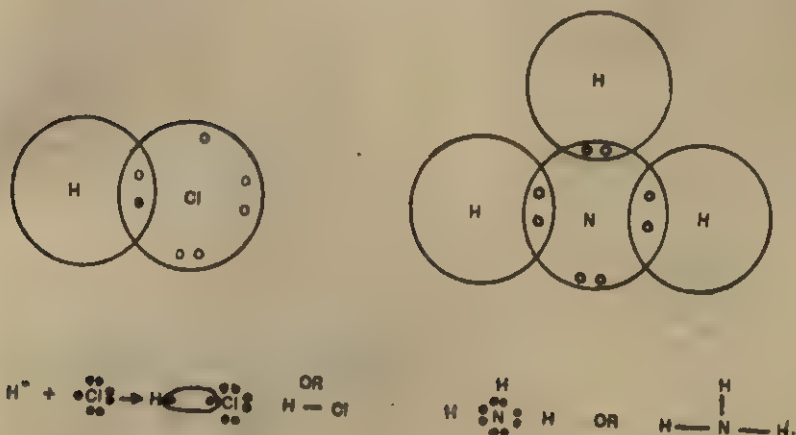


Fig. 6.15 Covalent bonding in a hydrogen chloride molecule

Fig. 6.16 Covalent bonding in ammonia molecule

Ammonia Molecule : Ammonia has three atoms of hydrogen and one atom of nitrogen. Nitrogen with five electrons in its valence shell and hydrogen with one electron in its only shell attain an octet and duplet electronic configurations respectively. Thus, three pairs of electrons are being shared between one nitrogen atom and three hydrogen atoms (Fig. 6.16). The Lewis structure and structural formula of NH_3 is also given in Fig. 6.16.

Methane Molecule has four hydrogen atoms and one carbon atom. The electronic configuration of carbon is 2, 4. Carbon shares its four electrons with four hydrogen atoms to attain stable electronic configuration like neon. In turn, every hydrogen atom also achieves duplet of

electrons. There are four shared pairs of electrons as shown in Fig. 6.17. The figure also includes the Lewis structure and structural formula of methane. The formation of a few other molecules through sharing of electrons is portrayed in Figs. 6.18 and 6.19.

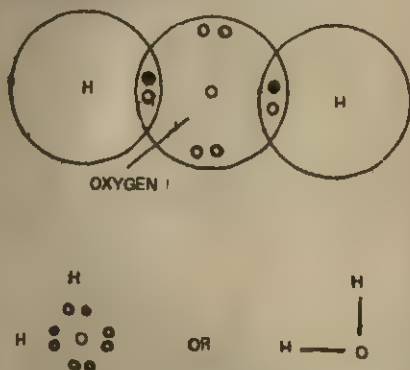
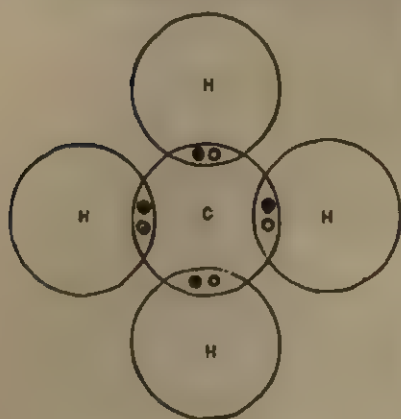


Fig. 6.18 Covalent bonding in water molecule

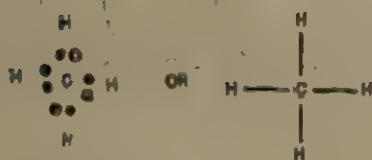


Fig. 6.17 Covalent bonding in methane

Multiple Covalent Bonds : In each of the examples discussed above, a single pair of electrons is shared between the constituent atoms in the given molecule. However, in some molecules, two or three pairs of electrons may be shared between atoms in order to attain a noble gas electronic configuration. When two or three pairs electrons are shared between two atoms in a molecule, the resulting bonds are called multiple covalent bonds. Two pairs of electrons between two atoms consti-

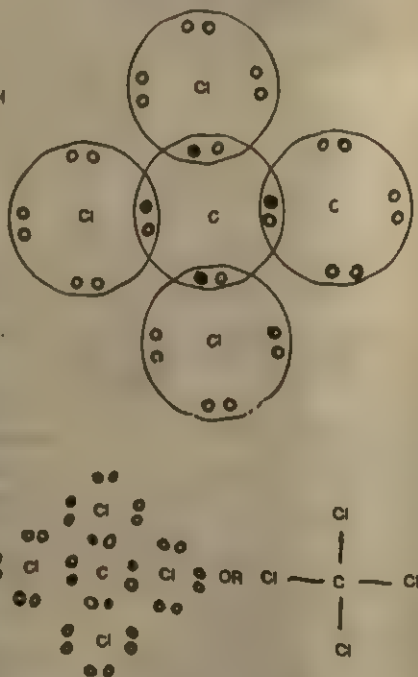


Fig. 6.19 Covalent bonding in carbon tetrachloride.

tute a double covalent bond which can be denoted by means of two dashes ($=$).

Similarly, three pairs of electrons between two atoms constitute a triple covalent bond which we denote by means of three dashes (\equiv).

Double and triple bonds occur in the Lewis structures of oxygen and nitrogen molecules respectively. Each atom in a molecule of oxygen contributes two electrons to form two shared pairs of electrons as given in Fig. 6.20.

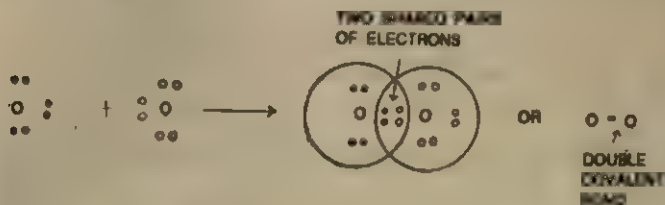


Fig. 6.20 Formation of oxygen molecule

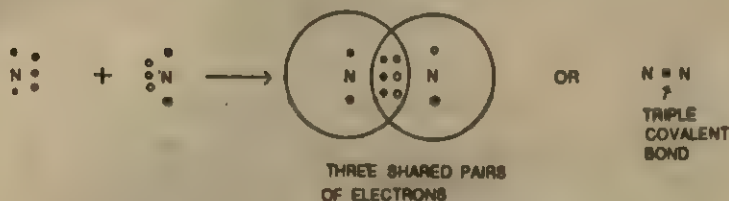


Fig. 6.21 Formation of nitrogen molecule

Similarly, each atom in a molecule of nitrogen shares three of its electrons with the other nitrogen atom to form a triple bond (Fig. 6.21).

The following covalent compounds also illustrate double bond and triple bond formation in the molecules.

In carbon dioxide, each of the two oxygen atoms shares two electron pairs with a carbon atom. Thus, each of the two oxygen atoms forms two covalent bonds and the carbon forms four covalent bonds (Fig. 6.22).

Ethylene and acetylene illustrate double and triple bonds respectively. In ethylene molecule, each hydrogen atom is linked with the carbon atom through a single covalent bond and both the carbon atoms are linked with each other through a double bond (Fig. 6.23).

In acetylene molecule, each hydrogen atom forms one covalent bond with a carbon atom and each carbon atom forms a triple bond with the other carbon atom (Fig. 6.24).

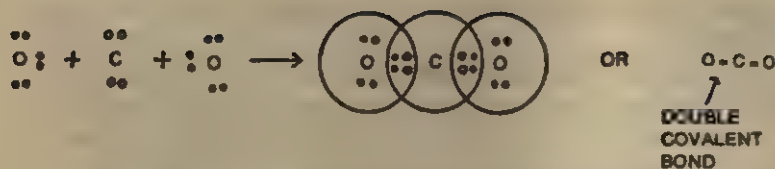


Fig. 6.22 Formation of carbon dioxide molecule

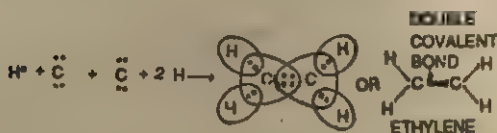


Fig. 6.23 Formation of ethylene molecule

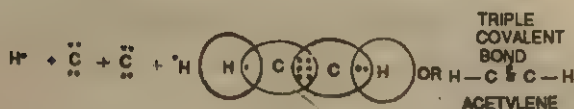


Fig. 6.24 Formation of acetylene

All the foregoing examples of covalent compounds reveal that the covalency of an element depends upon the number of electrons, its one atom contributes for forming a covalent bond.

Covalent bonds are, thus, formed,

1. between identical atoms,
2. between atoms belonging to the same periodic group such as chlorine and fluorine,
3. between atoms belonging to adjacent periodic groups such as aluminium and carbon, and
4. between any two non-metallic atoms such as carbon and oxygen ; hydrogen and chlorine; or boron and chlorine.

Properties of Covalent Compounds

1. Covalent compounds consist of molecules and do not contain ions.
2. Simple covalent compounds are volatile liquids or gases because their molecules are electrically neutral and their intermolecular forces are much weak.
3. They have low melting and boiling points, however, covalent solids like diamond and graphite are exceptions.

4. They are non-electrolytes and do not conduct electric current when in molten state or dissolved in water.
5. They are readily soluble in organic solvents such as CCl_4 , CHCl_3 , CS_2 , acetone, etc.
6. They are rarely soluble in water.

6.2.4 The Coordinate Bond

A covalent bond results from the sharing of two electrons between the combining atoms. Each atom contributes one electron to form the shared pair. It is also, however, possible to form a covalent bond where both the electrons are contributed by one atom. This is called a coordinate covalent bond or simply coordinate bond. It is illustrated by the following examples :

Formation of The Ammonium Ion : The formation of NH_4^+ ion can be portrayed by Lewis structure (Fig. 6.25). The lone pair of electrons

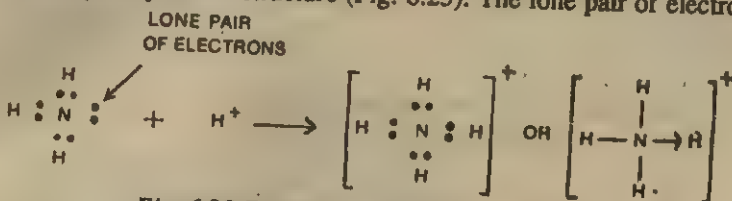


Fig. 6.25 Formation of coordinate bond

on the nitrogen atom is shared with H^+ ion. The atom that supplies the electrons (here the nitrogen) is called the donor atom and the atom that accepts the electrons (here the H) is called the acceptor atom. The coordinate bond is shown as an arrow (\longrightarrow) from the donor to the acceptor.

Other examples of coordinate bond are the formation of hydronium ion from water and a proton (Fig. 6.26) and the formation of

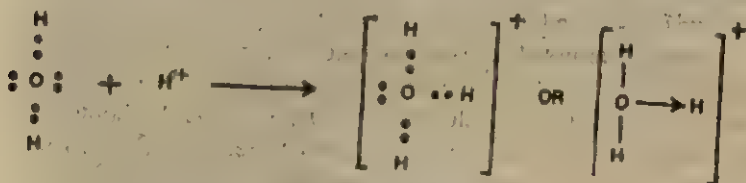


Fig. 6.26 Formation of hydronium ion, H_3O^+

deep blue $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion (obtained by adding ammonia to a solution of Cu (II) ions (Fig. 6.27).

Two or more stable molecules can also combine through a coordinate bond to yield a molecular complex. For example, nitrogen in ammonia can donate its lone pair of electrons present in the outer shell to electron deficient compounds such as BF_3 (Fig. 6.28) and AlCl_3 .

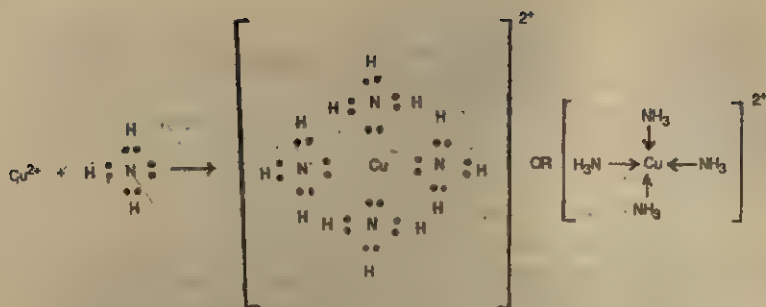


Fig. 6.27 Formation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion

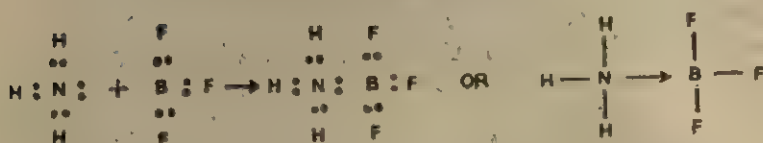
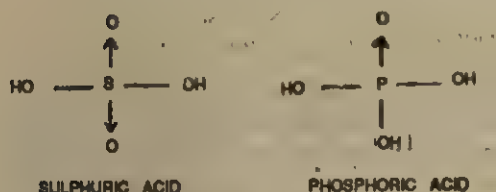


Fig. 6.28 Formation of the molecular complex, $\text{H}_3\text{N} \rightarrow \text{BF}_3$
(or $\text{H}_3\text{N} \longrightarrow \text{AlCl}_3$)

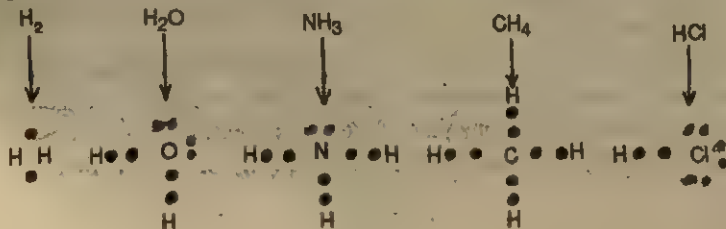


Certain compounds like sulphuric acid, phosphoric acid, etc. contain both covalent and coordinate bonds.

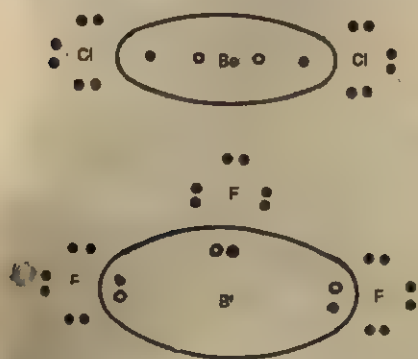
Exceptions to the Octet Rule

Although the octet rule is a very useful generalization in describing bonding, there are many substances for which it does not apply. We shall give a few exceptions here :

1. **Hydrogen molecule :** Hydrogen atom has only one electron in the first shell ($n = 1$). It requires one more electron to fill this shell, and thus, to have the same electronic arrangement as the noble gas helium. Both hydrogen and helium are, therefore, exceptions to the octet rule because only two electrons are required to fill the first energy level. Lewis dot structures for molecules containing hydrogen are given below :



2. **Atoms with less than eight electrons :** When an atom with less than four electrons in its valence shell shares them to form covalent bonds, it may not complete its octet by electrons sharing. Beryllium chloride and boron trifluoride can well illustrate this exception.



Beryllium chloride :

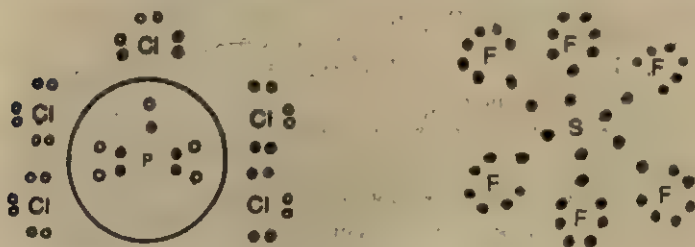
Be in BeCl_2 has only two valence electrons and can, therefore, form a maximum of two ordinary covalent bonds with two Cl atoms. The Lewis structure of BeCl_2 is given on the side. Around Be octet is incomplete; it is surrounded by only four electrons.

Boron trifluoride: When boron unites with three fluorine atoms, it forms BF_3 . The Lewis structure of the molecule is given above. Boron atom is surrounded by only six electrons.

Li^+ ion has a filled shell of two electrons, so the octet rule does not work well for this ion also.

3. **Atoms with more than eight electrons.**

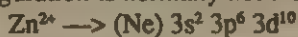
When an atom with more than four electrons in its valence shell shares them to form covalent bonds it may have more than eight elec-



trons. For example, when phosphorus unites with five chlorine atoms phosphorus pentachloride, PCl_5 , is formed. The Lewis structure of the molecule is given above. Phosphorus atom is surrounded by ten electrons. In SF_6 the central atom (S) is sharing 12 electrons. Lewis theory makes no provision for such cases.

4. We know that when the principal quantum number is 3 or larger, d orbitals are involved and the energy level can accommodate

more than eight electrons. When a transition element or post transition element such as Sn or Pb) forms a positive ion, the outershell electron configuration is normally not the same as that of noble gas, *e.g.*,



It is evident from the electronic structure of Zn^{2+} that its outershell $3s^2 3p^6 3d^{10}$, does not have the usual noble gas configuration $ns^2 np^6$. Thus, the octet rule fails for many metal ions.

6.3 SHAPES OF MOLECULES

Just as a photograph or sketch may fail to describe a person's appearance, electron dot structures and structural formulae fail to reflect the three dimensional shapes of molecules.

Molecules have various types of shapes. Some are long and thin, some are round, some are flat, some are rings and others are spirals. Apart from these, molecules also adopt linear, triangular, square planar, pyramidal, octahedral and other such dispositions. By shapes of molecules, we are meant, the way their atoms are arranged in space. The shapes of molecules affect many of their physical and chemical properties. In biological systems, complex molecules must fit together correctly for the chemical reactions to occur. The double spiral shape of the DNA molecule is associated with its function of transmitting information from one generation to the next. Some of the mysterious properties of water molecules are due to the angular shape of water. The properties of a substance basically depends upon its composition, *i.e.*, kinds of atoms. But geometric patterns of the atoms in a molecule and the nature and the strength of the bonds between them also affect their properties. The differences in the properties of the various allotropes of phosphorus - white, black and red - and sulphur - orthorhombic, monoclinic and plastic - are also related to the arrangement of the atoms and the bonds in them.

The ionic bonds, as we have already understood, arise due to purely electrostatic attraction between oppositely charged particles and is, therefore, non-directional. An ion attracts to itself as many ions of diverse nature as can be accommodated around it. The structure of ionic crystal is, therefore, determined primarily by the relative sizes of the ions. The covalent bonds, on the other hand, are directional. An atom forms covalent bonds only in certain specific directions. The shape, *i.e.*, geometric arrangement of the atoms in covalently bonded molecules and in crystals—depends on the directions of the covalent bonds.

Earlier the qualitative picture of the general arrangement of the atoms in a large number of molecules was deduced by studying the substances with the same molecular formulae but different properties. The reason for these different properties was attributed to the different

spatial arrangement of the atoms forming different molecules.

To-day, with the help of different experimental methods it is possible to determine the distance between atoms in a molecule or in a crystalline solid, the angles between bonds (bond angles), and thus, the geometry of a molecule. We will confine ourselves, in this unit, with the results of the experimental determination of the shapes of simple molecules and with the principles that govern their shapes. A simple theory enables us to predict the directions in which covalent bonds are formed, and therefore, to define the geometry of a molecule completely. It is called the VSEPR theory.

6.3.1 Valence Shell Electron Pair Repulsion (VSEPR) Theory

This theory was suggested by Sidgwick and Powell (1940) and later developed by R.J. Gillespie. The theory proposes that the geometric arrangement of atoms or groups of atoms about central atom is dictated by the number of electron pairs (lone pairs and bonding pairs) in the valence shell of the central atom. The geometrical shapes assumed by simple molecules are given in Table 6.1 with their electron dot structures and number of electron pairs associated with the central atom. These geometrical dispositions have been confirmed by electron diffraction studies.

TABLE 6.1

Name	BeCl ₂	B Cl ₃	CH ₄	NH ₃
Electron				
dot				
structure				
Number of electron pairs	2	3	4	4
Geometrical arrangement	Linear	Trigonal planar (Equilateral triangular)	Tetrahedral	Triangular pyramid or pyramidal

Name	H ₂ O	PCl ₅	SF ₆	IF ₇
Electron				
dot				
structure				
Number of electron pairs	4	5	6	7
Geometrical arrangement	V Shape	Trigonal bipyramidal	Octahedral	Pentagonal bipyramidal

In this theory, a multiple bond is regarded as equivalent to a single bond as far as molecular shape is concerned. The basis of the above configurations is that these electron pairs because of their negative charges keep themselves as far apart from each other as possible in shell so that the least repulsion occurs between them (has its origin in the Pauli's exclusion principle). Regular molecular shapes are obtained only when all the electron pairs are used as bonding to similar atoms. If some of the atoms are different, deviations from these regular shapes occur.

When the central atom carries one or more lone pairs of electrons (non-bonding pairs) the geometry of the molecule will depend upon the strength of the repulsion between electron pairs.

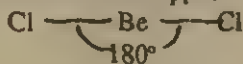
lone pair - lone pair > lone pair-bonding pair > bonding pair - bonding pair.

Repulsions between the bonding pairs in a species AB_n (when A is the central atom and n is the number of B atoms that attach to A by electron pair bonds) depend upon the difference in electronegativity between A and B, and decrease as the electronegativity of B increases.

These generalisations are very useful in explaining the shapes of simple molecules. Some simple molecules have been discussed below: From the Lewis structures for molecules, we can determine the number of electron pairs surrounding the central atom and the molecular shape resulting from the maximum separation of these electron pairs.

Linear Arrangement

Beryllium chloride : Beryllium chloride is a linear molecule (Table 6.1). The two electron pairs around the Be atom are mutually repulsive and orient themselves as far apart as possible to minimize repulsion and finally place themselves on opposite sides of beryllium atom at 180° bond angle.



The carbon dioxide molecule is linear since repulsion between the two electron pairs (bonding pairs) causes the oxygen atoms to be as far apart as possible. ($\text{O} = \text{C} = \text{O}$).

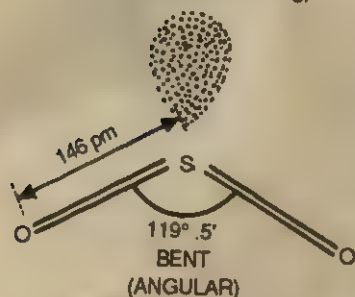
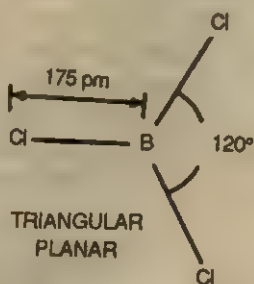
Linear nature can also be experienced through sp hybridization (to be discussed later) around beryllium and carbon atoms respectively.

Similarly, the other molecules such as carbon disulphide, beryllium halides, BeX_2 etc. are linear.

Trigonal Planar Arrangement

Boron Trihalides : Boron trichloride has a symmetrical triangular planar arrangement with a bond angle of 120° . The three bonding pairs

around a central atom repel each other and finally orient themselves at the corners of an equilateral planar triangle to achieve maximum separation. Boron atom assumes sp^2 hybridization (to be discussed later) and thus, confirms the shape of BCl_3 molecule. Other trihalides of boron also have a similar shape.



Sulphur Dioxide : Sulphur in sulphur dioxide molecule is attached to two oxygen atoms through double bonding pairs. There is one lone pair of electrons on the sulphur. Thus, the SO_2 is like an equilateral triangle with a bond angle of $119^\circ 5'$ which is in close agreement with an angle of 120° . It assumes angular shape because of presence of a lone pair of electrons. Later it has been confirmed by sp^2 hybridization around sulphur.

Tetrahedral Arrangement

Methane : In methane, the carbon atom is attached to four hydrogen atoms through four bonding pairs of electrons. These bonding pairs of electrons repel each other giving

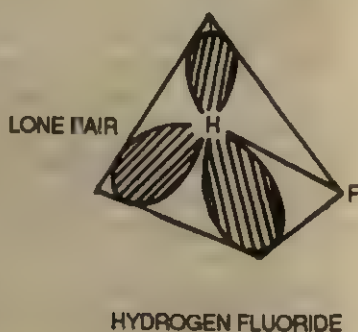
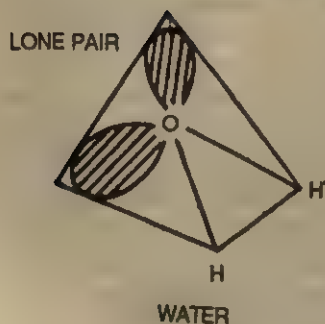
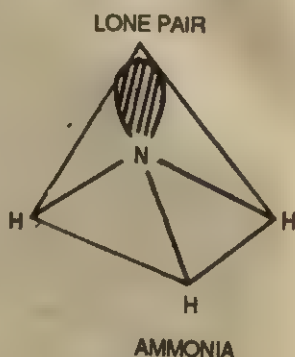
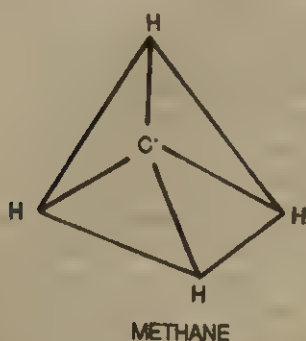
a regular tetrahedral shape with a bond angle of $109^\circ 28'$. Ammonium ion, NH_4^+ , has this shape.

Ammonia : In ammonia, the nitrogen atom has four pairs of electrons around it. Only three of these electron pairs have hydrogen atoms attached to them. The fourth pair of electrons is a lone pair. It assumes the shape of triangular pyramid with $106^\circ 45'$ as bond angle which is very close to tetrahedron angle. This distortion and decrease in bond angle is caused by the greater repulsive effect of a lone pair of electrons upon the remaining three bonding pairs of electrons. The triangular pyramid is not a regular tetrahedron, because its faces are not equilateral triangles. Only the face occupied by three hydrogen atoms is an equilateral triangle.

These characteristics of the shape of NH_3 molecule will be explained later on the basis of orbital overlap and hybridization concept. PCl_3 , NF_3 and H_3O^+ also adopts the triangular pyramid shape. Here also, two corners of the tetrahedron are occupied by two atoms and the remaining two corners by non-bonding electrons. Bond angles are different in each case because of the electronegativity differences in the atoms involved.

Water : In water, the oxygen atom has four pairs of electrons around it. Only two of these electron pairs have hydrogen atoms attached to them. The water molecule has two lone pairs of electrons. A tetrahedron is the most probable arrangement for four groups of electrons about the central atom. The lone pairs of electrons have a very strong repulsive and compressive effect upon two bonding pairs of electrons and the bond angle further decreases to $104^{\circ} 27'$ which is very close to tetrahedron angle. Water molecule has an angular shape (V shape).

The shape will be explained later on the basis of orbital overlap and hybridization concept. Other molecules / species with a similar shape are H_2S , F_2O , NH_2^- and SCl_2 . Bond angles in each is different because of the difference in electronegativity of the atoms attached to the central atom.



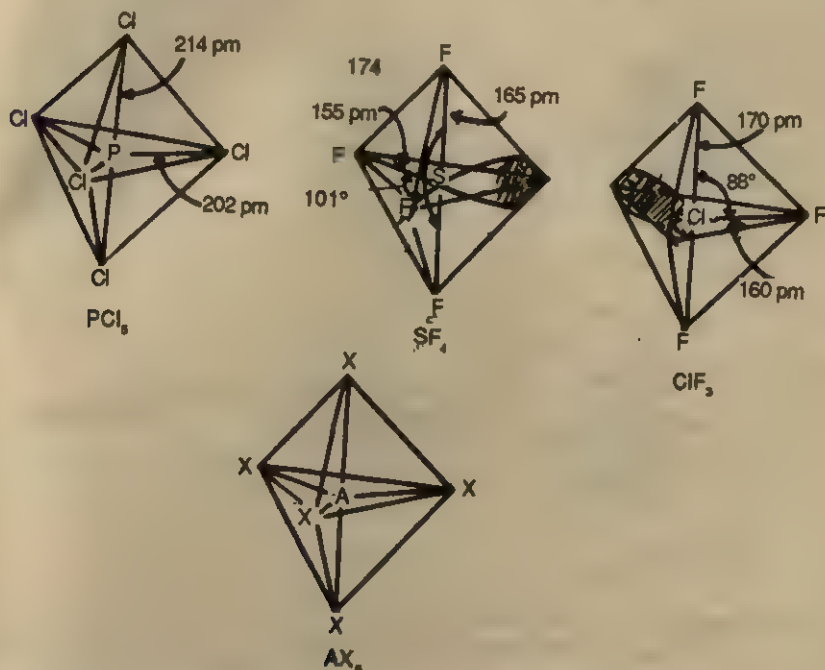
Hydrogen fluoride : If only one atom is attached to the central atom as in HF, HCl, HBr or HI, the molecular shape is, of course, linear irrespective of the number of electron pairs involved.

Trigonal Bipyramidal Arrangement

When the central atom in a molecule is surrounded by five pairs of electrons, maximum separation is achieved by trigonal bipyramid

geometry. This shape consists of two triangular pyramids that share a base (face). It has six equivalent triangular faces, nine edges and five vertices. Although the faces are all equivalent triangles, they are not always equilateral triangles as in the tetrahedron and octahedron. In a molecule, with such a shape, say phosphorus pentachloride PCl_5 , three bonds lie in a plane with 120° bond angles and are designated equatorial. The other two bonds are directed oppositely along the axis perpendicular to this plane, and thus, are at angles of 90° (called axial angles) to the equatorial set.

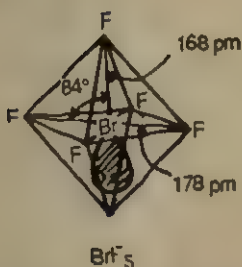
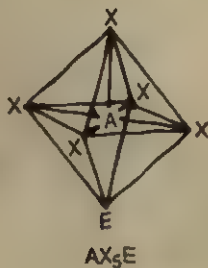
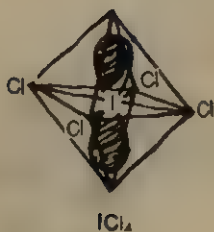
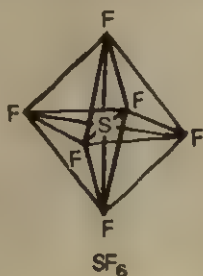
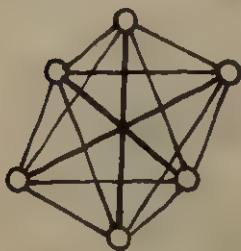
Other molecules/species with five pairs of electrons but with different shapes because of the presence of non-bonding pairs are given below : SF_4 (see saw shape) BrF_4^+ , (see saw), ClF_3 (T-shape) and BrF_3 (T-shape), etc.



Octahedral Arrangement

Six electron pairs surrounding an atom orient themselves at angles of 90° in an arrangement called octahedron, or octahedral. This shape has six equivalent vertices, 12 equivalent edges and 8 equilateral triangular faces. Since the positions are all equivalent, a non-bonding pair of electrons can occupy any of the six positions. If two non-bonding pairs are available, they arrange themselves at an angle of 180° . A molecule of SF_6 has this shape. Other molecules/species

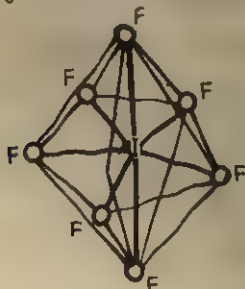
with six pairs of electrons but with different shapes are given below: BrF_5 and IF_5 (one non-bonding pair; square pyramidal), XeF_4 , BrF_4 and ICl_4^- (two non-bonding pairs; square planar).



E = LONE PAIR OF ELECTRON















Pentagonal Bipyramidal Arrangement

Iodine heptafluoride with seven pairs of electrons has this shape. BrF_6^- ion has distorted octahedral shape (one non-bonding pair)



The molecular shapes deduced by the VSEPR theory have been supported by electron diffraction studies. The molecular shapes we have discussed to this point are summarized in Table 6.2.

TABLE 6-2 Shapes of molecules predicted from electron-pair repulsion theory of directed valence

Total number of electron pairs on central atom	Molecular shape	Co-ordination number of central atom	Types of electron pairs on central atom	Formula	Most stable configuration	Examples
2	Linear	2	2 BP	AX_2	Linear 	$HgCl_2, CdI_2, [Ag(CN)_2]^-$
3	Triangular	3	3 BP	AX_3	Equilateral triangle 	BF_3, BI_3, GaI_3
		2	2 BP, 1 LP	AX_2E	V-shaped 	$SnCl_2, PbCl_2$
4	Tetrahedral	4	4 BP	AX_4	Tetrahedral 	$CH_4, [BF_4]^-, SnX_4$
		3	3 BP, 1 LP	AX_3E	Trigonal pyramidal 	$NH_3, H_3O^{+}, PH_3, AsH_3$
		2	2 BP, 2 LP	AX_2E_2	V-shaped 	H_2O, H_2S
		1	1 BP, 3 LP	AXE_3	Linear 	HF, HCl
5	Trigonal bipyramidal	5	5 BP	AX_5	Trigonal bipyramidal 	$PCl_5, SbCl_5$
		4	4 BP, 1 LP	AX_4E	Irregular tetrahedron or (see-saw) 	$SF_6, TeCl_6$
		3	3 BP, 2 LP	AX_3E_2	T-shape 	ClF_3, BrF_3
		2	2 BP, 3 LP	AX_2E_3	Linear 	$[ICl_2]^{-1}I_2$
6	Octahedral	6	6 BP	AX_6	Octahedral 	$SF_6, [SiF_6]^{2-}, [PbCl_6]^{2-}$
		5	5 BP, 1 LP	AX_5E	Square pyramidal 	BrF_5, IF_5
		4	4 BP, 2 LP	AX_4E_2	Square planar 	$[ICl_4]^{-1}(BrF_4)^{-1}$

E = Lone pair of electrons

Figure 6.29 shows the electron charge cloud models of CH_4 , NH_3 , H_2O and HF . From what we have discussed so far it is clear that it is the number of regions of negative charge (not the number of bonds) surrounding the central atom which dictates the shape of a molecule. Thus, both carbon dioxide, CO_2 ($\text{O}=\text{C}=\text{O}$) hydrocyanic acid HCN ($\text{H}-\text{C}\equiv\text{N}$) with two negative centres around their central atoms (C) are linear with respect to negative centres and atoms as well. According to one of the assumptions of VSEPR theory each double bond in CO_2 is equivalent to a single negative centre. Similarly the triple bond in HCN is taken as one single negative centre. Sulphur

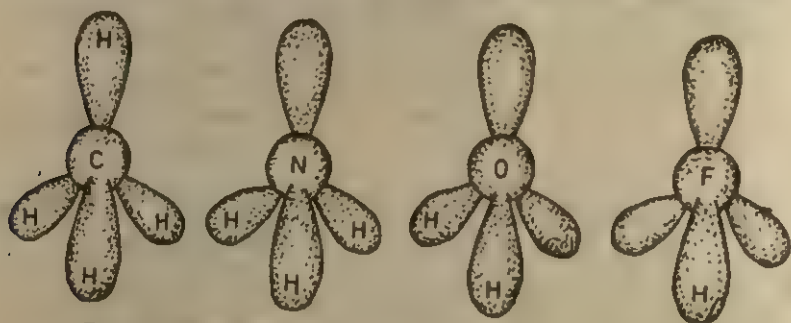


Fig.6.29 Electron charge cloud models of molecules

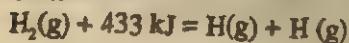
dioxide, SO_2 has three negative charge centres around the S atom and is V-shaped with respect to atoms.

6.4 QUANTUM THEORY OF THE COVALENT BOND

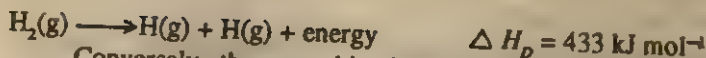
We have so far described the simple picture of a covalent bond as a pair of electrons shared between two atoms. Further VSEPR theory proved to be a useful device for predicting the molecular shapes of different types of molecules, but it still does not answer the basic questions. How do atoms share their valence electrons? How are these electrons able to avoid each other? To find the plausible answers, we turn now to a deeper view of the covalent bond on the basis of quantum theory. This theory, particularly the quantum mechanical ideas such as orbital concept and Pauli's exclusion principle, has already established its superiority to know the behaviour of electron. Just as it has been found convenient to study the electronic structure of atoms in terms of the hydrogen atom, the simplest atom—it will be appropriate to start with the hydrogen molecule (H_2) - the simplest molecular system.

6.4.1 The Hydrogen Molecule

It has been found that 433 kJ of energy is required when one mole of hydrogen molecule on heating dissociates into hydrogen atoms.



or



Conversely, the recombination process of hydrogen atoms releases 433 kJ of energy. Then it can be concluded that the recombination of hydrogen atoms is a favourable reaction as it leads to a stable molecule. This phenomenon is not simply confined to a hydrogen molecule, it is as well applicable in the case of other molecules. Thus, a molecule has always lower energy as compared to isolated atoms.

What makes a hydrogen molecule more stable than two isolated hydrogen atoms?

In 1927, Walter Heitler and Fritz London applied the concept of quantum mechanics to the electron pair representing a covalent bond. For the hydrogen molecule, the Heitler London valence bond model pictures the two isolated hydrogen atoms combining together to share a pair of electrons.

This treatment has been further advanced by Linus Pauling and Slater to incorporate directional orientation of the bond in space leading to an accurate picture of the geometry of the molecule. The valence bond approach may be illustrated qualitatively by considering the hydrogen molecule.

Consider two individual hydrogen atoms as represented by two atomic orbitals (1s) with one electron in each at an infinite distance (Fig. 6.30).

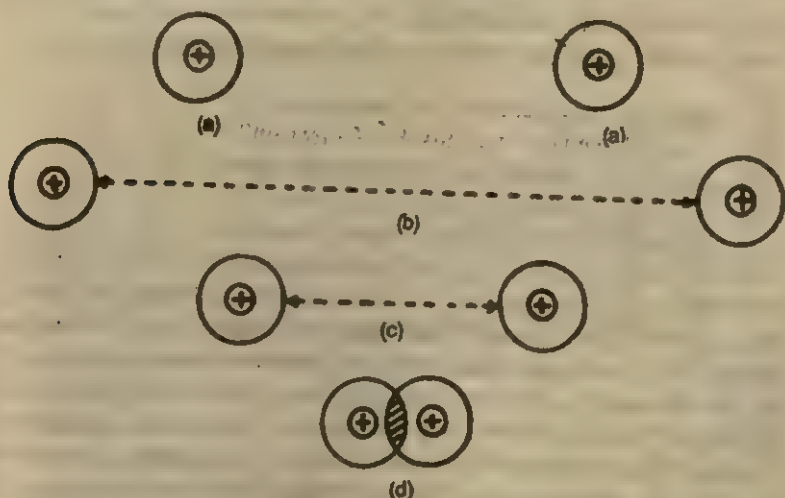


Fig. 6.30 Formation of hydrogen molecule : (a) a simple representation of the two isolated hydrogen atoms (shown as orbitals), (b) two hydrogen atoms at an infinite distance, and hence, no interaction, (c) when the two atoms come closer—interaction starts, and (d) two hydrogen atoms as in H_2 molecule

At large internuclear distance (Fig. 6.30(b)) the total energy is simply $E_A + E_B$, the energy of the separated atoms as there is no interaction between the two atoms at such distances. Because no chemical bond formation is possible, there is no drop in energy. Hence, no stability results. The situation, however, takes a new turn as the two hydrogen atoms approach one another (Fig. 6.30(c)), each attracts the other's electron. This attraction of the two electrons by the two nuclei helps in bringing the atoms closer (Fig. 6.30(d)).

When two atoms approach one another closely, both attraction and repulsion take place.

In the formation of hydrogen molecule, the following interactions (coulombic attractions and repulsions) are possible (Fig. 6.31). The diagram shows the two atoms at an instant, when one electron from each of them is in the region of overlap.

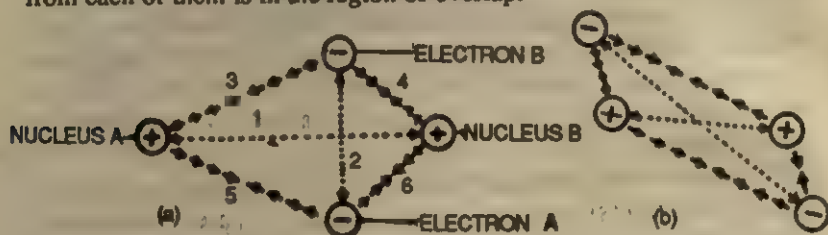


Fig. 6.31 Schematic diagram of the H_2 molecule representing the coulombic forces $\rightarrow \rightarrow \leftarrow \leftarrow$ of attraction and repulsion (dashed lines)

- (i) attraction between nucleus A and electron A
- (ii) attraction between nucleus A and electron B
- (iii) attraction between nucleus B and electron B
- (iv) attraction between nucleus B and electron A
- (v) repulsion between electron A and electron B
- (vi) repulsion between nucleus A and nucleus B

Of course, the electrons A and B are moving all the time, so will not always be in the overlap region as shown in Fig. 6.31 (a). This does not matter. The same type of forces will always be present as shown in Fig. 6.31 (b). Sometimes the repulsive forces between two atoms are stronger than the attractive forces, so the atoms get separated. Sometimes the attractive forces are stronger than the repulsive forces and the atoms continue to be together. At this stage, it is said that a chemical bond has been formed.

The interaction (vi) deals only with the two nuclei while the interactions (i) to (v) deal with the electrons and nuclei. Hence, broadly the formation of H_2 can be considered into two parts :

(a) the change in energy due to the forces, (i) to (v) as the internuclear distance decreases,

(b) the change in energy due to the internuclear repulsion (vi) as the internuclear distance decreases.

The change in energy due to (i) to (v) should be such that compensates for the increase in energy due to internuclear repulsion in the case of (vi). The net drop in energy will result in bond formation.

The energy changes which take place when two neutral hydrogen atoms are brought together from a large distance to form a hydrogen molecule are portrayed in Fig. 6.32.

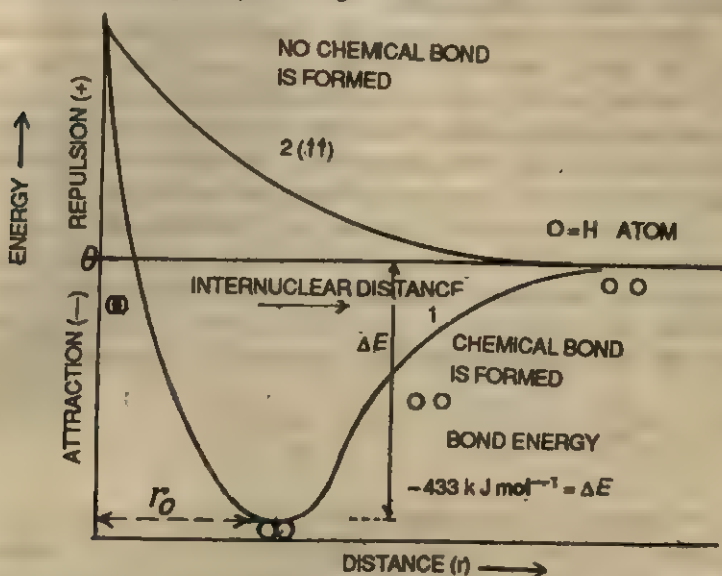


Fig. 6.32 Energy variation with internuclear distance in the formation of hydrogen molecule

At large internuclear distances, the two hydrogen atoms neither attract nor repel, hence, the energy of interaction of two H atoms is zero. When they approach one another (spins of the two electrons associated with atoms are opposed), they begin to attract. As this attraction becomes stronger and stronger, the potential energy (kinetic energy is ignored as motion of the two atoms is taken into consideration) gets lower and lower. This continues upto a certain distance, r_0 (equilibrium distance) at which the potential energy no longer decreases. As r continues to decrease, the potential energy begins to rise due to the action of repulsive force repulsion between the two positively charged nuclei which is of considerable magnitude at small internuclear distance (line 1).

If the approaching atoms have electrons with parallel spins, the potential energy increases continuously as the atoms are brought together (line 2). In this case, the repulsive force (repulsion of the electrons) predominates at all values of r and the potential energy curve continuously rises.

The equilibrium distance, r_0 , which corresponds to the minimum potential energy (i.e., the maximum stability) is called the **bond length**. For H_2 molecule, r_0 is found to be 74 pm. Clearly this is the minimum distance at which two atoms experience a maximum mutual attraction and are bound together.

The energy corresponding to this minimum is called **bond energy**. Thus, energy equivalent to bond energy, should be sufficient to break the bond as well. Under the circumstances, in a molecule containing one bond only, the **dissociation energy** is equal to the bond energy. From the curve, bond energy comes out to be the difference between the minimum energy and the energy of the isolated atoms.

Thus, when two hydrogen atoms having electrons with antiparallel spins approach one another, a chemical bond is formed. Now, there are two possible equivalent structures (I and II) which are indistinguishable, once the bond has been formed. This is because of the possibility of interchange of electrons between the two atoms.



The bond formation is due to the fact that if the electrons have antiparallel spins their movement about both nuclei becomes possible. This sort of movement brings about a considerable increase in the density of the electron cloud in the space between the two nuclei. Attraction occurs between the nuclei and a region with a high density of negative charge results. The attraction reduces the potential energy of the electrons and consequently the potential energy of the system, and a chemical bond results.

Chemical Bond in Hydrogen Molecule

From the inception of a molecule, it has been thought that atoms in a molecule are joined by bonds, shown by a dash (—) between the atoms. Thus, H_2 molecule is written as $H - H$. The nature and origin of such chemical bonds has now been established. A bond is formed as a result of attraction and repulsion of the electrons and the nuclei. Hydrogen molecule could be in existence because of the attractive forces between each nucleus and two electrons and those between each electron and two nuclei. The two electrons are a kind of mortar that binds the two nuclei together. One may say that the pair of electrons shared by the two nuclei is the chemical bond. This shows the bearing effect of electron pairs in the Lewis structure. Thus, a 'dash' between two atoms which designates a chemical bond as per older formulation corresponds to a shared period of electrons in the modern approach. This shared pair of electrons is called a covalent

bond. When the two atoms involved are the same, *e.g.*, H_2 , O_2 , N_2 , *etc.* the electron pairs are shared equally and the bond is a **non-polar covalent bond**. However, when two different atoms form a covalent bond, the electron pairs are shared unequally and the bond is called a **polar covalent bond** (or a **polar bond**).

Orbital (s - s) in Bond Formation

The formation of the chemical bond has been well explained in the terms of the lowering of the potential energy of the electrons resulting from the increased density of the electron cloud (electron orbital) in the internuclear region.

Fig.6.33 shows the distribution of electron density in the interaction of 1s orbitals on hydrogen atoms to form the hydrogen molecule.

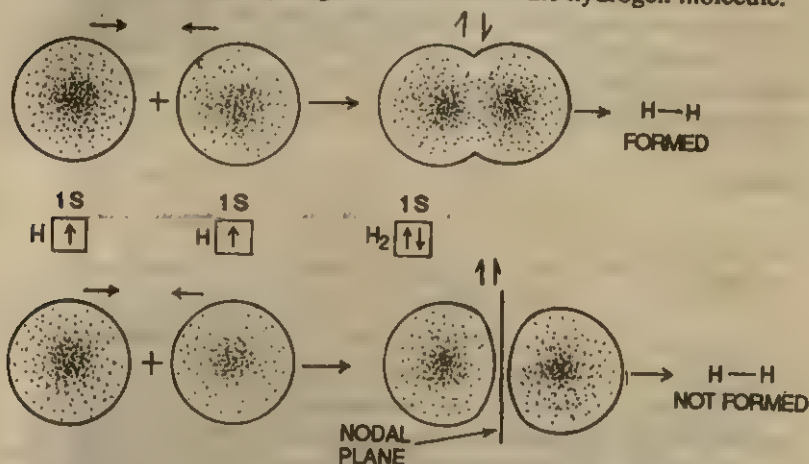


Fig. 6.33 The interaction of 1s orbitals on hydrogen atoms to form hydrogen molecule: (a) Antiparallel spins - atoms combine to form a molecule, and (b) parallel spins - atoms are repelled


As a result of combining of two atomic orbitals containing electrons with antiparallel spins, the density of the electron cloud between the nuclei increases. In this case the electron clouds (orbitals) are said to be overlapping. Thus, electron clouds stretch out towards one another and a chemical bond is formed. On the contrary, in case of electrons with parallel spins, the density of the electron cloud between the atoms falls to zero, because the electrons are forced out of the region between the nuclei and a chemical bond is not formed. Thus, we conclude that the orbital overlap is necessary for a chemical bond to be formed and the two electrons forming the bond must have opposite spins (Pauli's exclusion principle).

Now at this stage the question arises as to whether or not H_3 , H_4 , etc. molecules are possible? In the orbital overlap of H_2 molecule both the available electrons (one from each atom) are used. Thus, no additional electrons are available with H_2 molecule to combine with more hydrogen atoms. Therefore, only H_2 exists but not H_3 , H_4 , etc.



Like H_2 molecule, helium does not exist as He_2 . This is because when the two helium atoms approach one another, no drop in potential energy is possible and consequently no bond formation takes place. In the helium atom, 1s orbital is full to its maximum capacity. The Pauli's exclusion principle, therefore, does not permit a saturated 1s orbital of helium atom to overlap with that of the other atom. Helium is thus found in the monoatomic state, He.







6.4.2 Sigma (σ) and Pi (π) Bonds and Some Simple Molecules

In this section, our discussion will pertain to molecules formed by atoms of the second row elements of the periodic table.

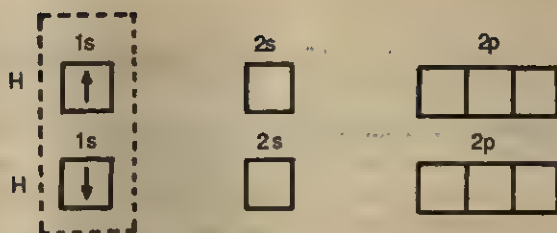
To make the involvement of orbitals in chemical bonding, we shall show orbitals by square boxes of the type . Orbitals are usually arranged in order of increasing energy as follows:

Orbitals	1s	2s	2p
Pictorial picture of orbitals			

A group of three 2p boxes represents the three 2p orbitals with equal energy (degenerate). An empty box represents a vacant orbital, i.e., no electron is present. A box with a single arrow '' represents the presence of one electron (a singly occupied orbital) whereas a box with two arrows () represents the presence of two electrons with antiparallel spin (a doubly occupied orbital). A pictorial representation of a single hydrogen and helium atoms, i.e., their electronic structures are given below:

	1s	2s	2p
H			
	1s	2s	2p
He			

The overlapping of orbitals to produce a chemical bond is shown below by enclosing the appropriate orbitals within a rectangle. The pictorial diagram for a hydrogen molecule is,



The process of formation of H_2 molecule as understood through the s-s overlapping is given in Fig. 6.34.

S-S OVER LAPPING

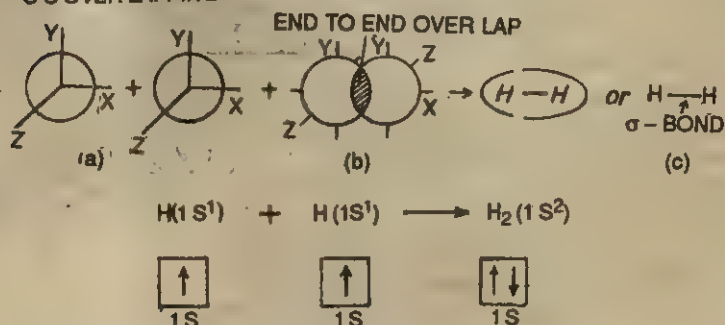


Fig. 6.34 Formation of hydrogen molecule through s-s-overlapping : (a) separate s orbitals, (b) end to end overlapping of s orbitals, and (c) sigma bond orbitals (s-type)

The bond formed by this type of orbital overlap is called a σ bond. Thus, σ bond is obtained by overlapping of the orbitals along the internuclear axis (end to end overlap). In such bonding, rotation of one atom relative to the other about a line joining the two atoms does not alter the extent of overlap of the two orbitals. Thus, free rotation is possible about a σ bond.

Three types of overlapping, viz., s-s overlapping, p-p overlapping and s-p overlapping are possible which lead to σ bond formation. These overlappings are illustrated in the formation of H_2 (Fig. 6.34) F_2 (Fig. 6.35), and HF (Fig. 6.36) molecules.

Fluorine Molecule : A fluorine atom, with the electronic configuration, $1s^2, 2s^2, 2p^5$ is shown below through its pictorial representation.



One of the 2p orbitals is only half-filled. A fluorine atom can combine with another fluorine through the overlapping of the two half-filled 2p orbitals. In the process, two fluorine atoms gain stability

and share a pair of electrons. Thus, a pair of electrons forms a single bond.

The formation of a stable bond (Fig. 6.35) due to the overlap of electron clouds (p-p) has been pictured schematically in terms of the pairing of electron-spins from each atomic orbital involved in bond formation as illustrated below for F_2 molecule.

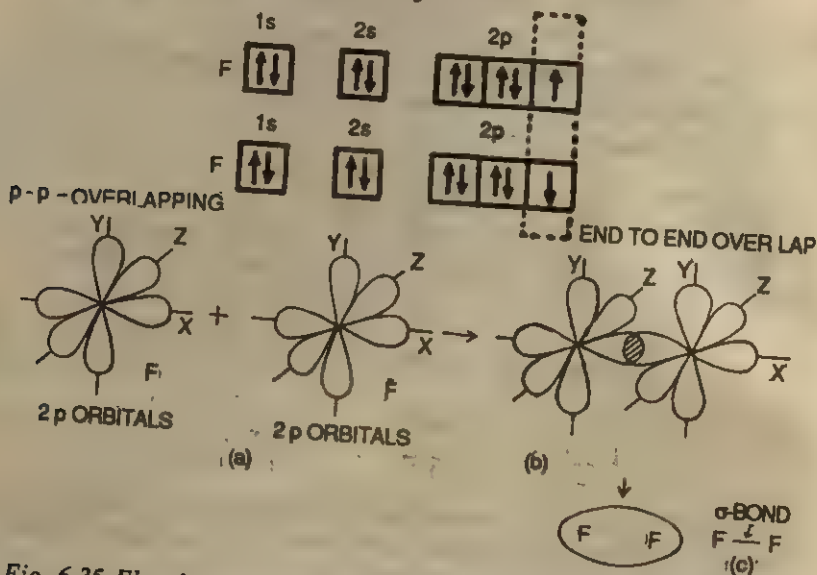


Fig. 6.35 Fluorine molecule : (a) Separate p orbitals, (b) end to end overlapping of p and p orbitals, and (c) sigma bond orbitals (p-p)

Again a σ bond is formed. The process shows that each fluorine atom has one unpaired electron in one of the 2p orbitals. So when two fluorine atoms approach each other, the two half-filled 2p orbitals overlap and share a pair of electrons. The remaining lobes will not be used for further overlapping since the 2p orbitals of both the fluorine atoms have now become part of bonding orbital uniting both the fluorine atoms.

Both H_2 and F_2 molecules have single bonds between their atoms which result from sharing of an electron pair. The difference is that the electron pair in H_2 results from the overlap of 1s orbitals whereas in F_2 from the overlap of 2p orbitals. In the process of overlap and thus sharing of electrons, each hydrogen atom acquires two electrons which is the maximum capacity of the 1s orbital and similarly each fluorine atom acquires eight electrons in its valence shell which is the maximum capacity the s and p orbitals contained in second energy level ($n = 2$). It is also worthnoting that besides one pair of bonding electrons, each fluorine atom has three pairs of valence electrons (lone pairs) not associated with any other atom.

Hydrogen Fluoride, HF Molecule

When a molecule of hydrogen fluoride is formed, the s orbital of hydrogen overlaps with the half-filled fluorine p orbital. This involves s - p overlapping. The various stages for the formation of a single covalent bond in HF are shown in Fig. 6.36.

Figure 6.36 shows that all the three 2p orbitals are at right-angles to one another. It also illustrates the way the bonding orbital of the fluorine atom overlaps with the s orbital of hydrogen. Water and ammonia also involve the s-p overlapping.

Again a σ bond is formed - only one lobe of the 2p orbital (singly occupied) overlaps the hydrogen 1s orbital. The remaining two lobes may not be used for further overlapping since the 2p orbital has

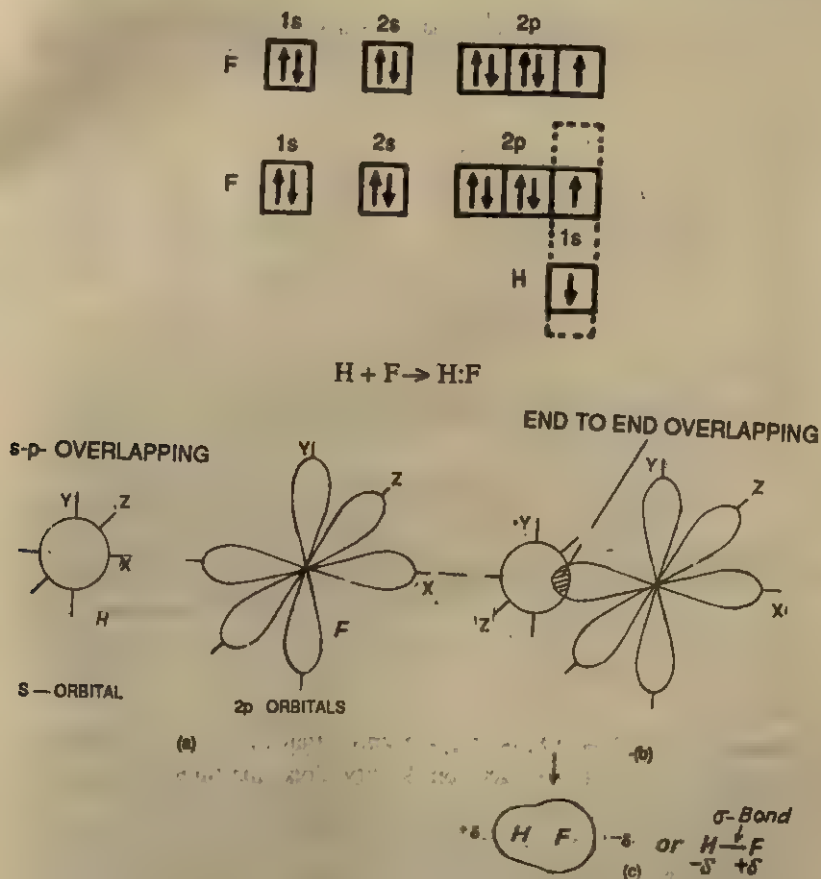


Fig. 6.36 HF molecule: (a) Separate s and p orbitals, (b) end to end overlapping of s and p orbitals, and (c) sigma bond orbitals, (s-p) types.

now become a part of the bonding orbital embracing both hydrogen and fluorine atoms.

Unlike the hydrogen bonding orbital the bonding orbital of HF is assymmetrical. Because of the large difference between the electronegativities of H and F the shared bonding electrons shift towards the fluorine atom. This brings about a slight separation of charge leaving the hydrogen end of the molecule with a small positive charge (δ^+) and the fluorine end with a small negative charge (δ^-). Thus, HF is a polar molecule.

Electronegativity : It is a measure of the attraction that an atom has for a shared pair of electrons in a molecule. The larger the value, the greater is the ability of an atom to attract electrons to itself. Table 6.3 includes the electronegativities of some common elements. Electronegativity values have only relative significance.

TABLE 6.3 Electronegativity values for atoms of common elements

H 2.1							He 0.0
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne 0.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar 0.0
K 0.8	Ca 1.0					Br 2.8	Kr 0.0
Rb 0.8						I 2.4	
Cs 0.0							

Water Molecule, H_2O

The oxygen atom has the electronic configuration $1s^2, 2s^2 2p^4$. The four $2p$ orbital electrons are distributed among the three p orbitals as dictated by Hund's rule $2p_x^2, 2p_y^1, 2p_z^1$. The two orbitals with one unpaired electron each overlap with the two $1s$ orbitals of hydrogen. The formation of a stable bond due to the overlap of electron clouds can be pictured schematically in terms of pairing of electron spins from each atomic orbital involved in bond formation is given in Fig.6.37.

Bond Angle, $H - O - H$: We know that the three $2p$ orbitals of oxygen have maximum electron density along the three mutually perpendicular axes directing towards the space. Two bonds are formed between oxygen and two hydrogen atoms when two spherically symmetrical $1s$ orbitals (electron cloud) overlap the two p orbitals of oxygen (Fig. 6.37). A stable bond can only be expected from the maxi-

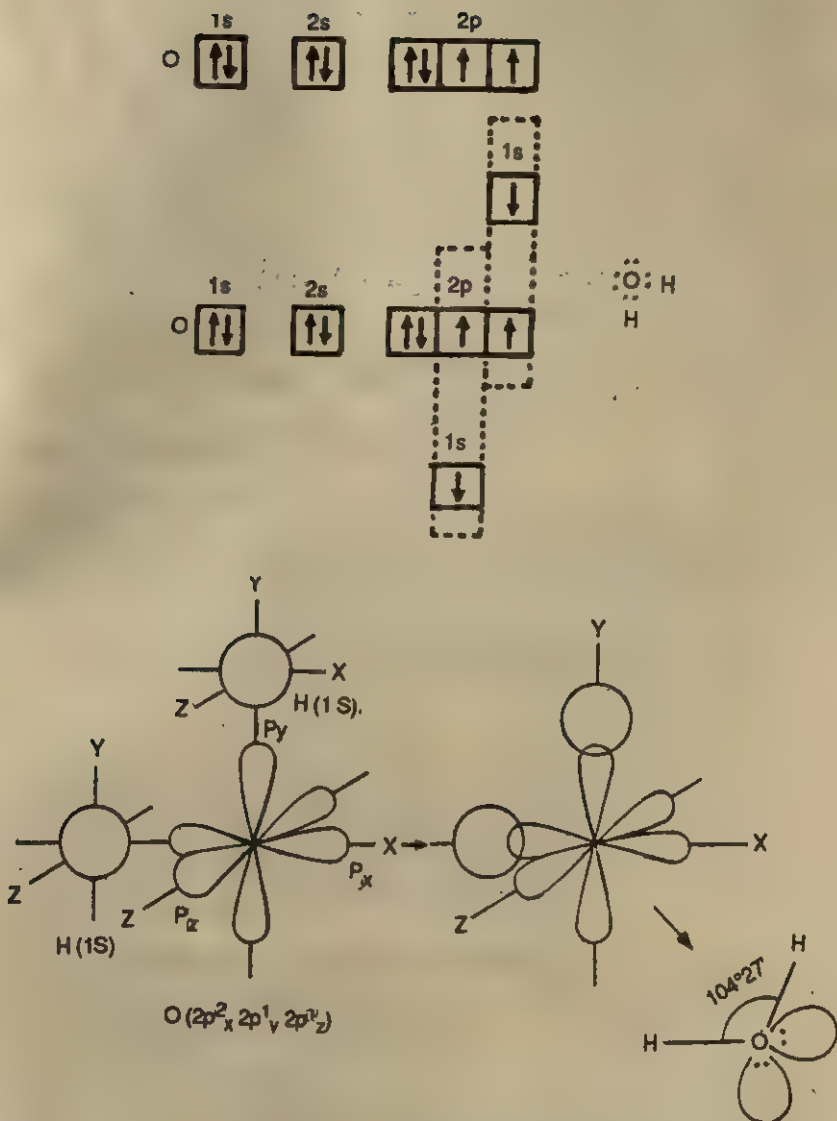


Fig. 6.37 Water molecule : (a) Separate s and p orbitals, (b) end to end overlapping of two s orbitals and p orbitals forming sigma bond (s-p) type, and (c) V-shape of water with bond angle, $\text{H}-\text{O}-\text{H}$ $104^\circ 27'$

imum overlap and this will be possible only if the two p orbitals involved in overlap are perpendicular to each other. If oxygen uses two p orbitals (p_x and p_y) which are at right angle to each other, a 90° angle between the two bonds in H_2O molecule is expected. However, this angle has been found experimentally to be $104^\circ 27'$. This discrep-

ancy can be explained on the basis of a strong affinity of oxygen for these bonding electrons. Thus, the atoms in a molecule of water are held together by bonds that are somewhat polar because oxygen becomes more electronegative due to its strong affinity for bonding electrons. This leads to a greater relative concentration of negative charge around oxygen atom. As a result, the oxygen atom acquires partial negative charge, δ^- and each hydrogen atom a partial positive charge, δ^+ . These positively charged hydrogen atoms repel each other and thereby the bond angle is enlarged. Water molecule and its shape has already been discussed on the basis of VSEPR theory. Both the approaches for the shape of the water molecule predict angular molecule. The present and the alternate idea involve two sigma bonds, each of which arises from the overlap of one s atomic orbital of hydrogen with a 2p atomic orbital of oxygen.

The following points have emerged from the examples discussed so far :

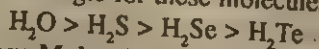
1. The covalent bonds between atoms arise when the unpaired electrons in the original atoms get paired. The number of covalent bonds depend upon the number of unpaired electrons present in the central atom.
2. The geometrical shape of the molecule is determined by the orientation of the overlapping atomic orbitals of the bonded atoms.

Hydrides of Group 16

Hydrogen sulphide (H_2S), hydrogen selenide (H_2Se) and hydrogen telluride (H_2Te) assume the geometrical shape of water. On descending the group, the bonding orbitals become larger and more diffuse and overlap less favourably with the hydrogen 1s orbitals. This means that the hydrogen atoms in H_2S , H_2Se and H_2Te are more separated. Repulsion, therefore, is less, and the bond angles in these molecules become close to 90° .

Further on descending the group, the electronegativity decreases in the order $\text{O} > \text{S} > \text{Se} > \text{Te}$, so does the polarity of the molecules.

This suggests that the charge separation in MH ($\text{M} = \text{O}, \text{S}, \text{Se}$ or Te) decreases from OH to TeH . As a result, the positively charged hydrogen atoms experience repulsion in a decreasing fashion. Hence, the bond angle for these molecules decreases in the order

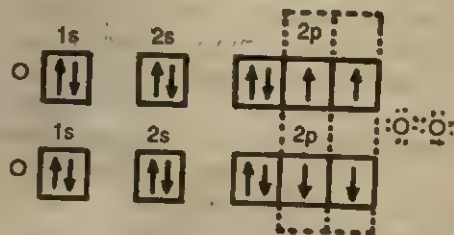


Oxygen Molecule, O_2

The double and triple bonds encountered in many chemical compounds are combinations of sigma and pi bonds. Generally, pi bonds are more reactive than sigma bonds. Covalent bonding between dumb-bell shaped p orbitals can occur in two ways. If the p orbitals overlap end to end a sigma bond results. However, p orbitals can also

overlap side to side resulting in a different electron distribution, a pi bond. This has been illustrated in Fig. 6.38 in the formation of O_2 molecule.

When two oxygen atoms combine, the sharing of two pairs of electrons between the two atoms takes place. This structure would give each oxygen atom a completed octet of electrons in its outershell and would show that all electrons are paired. The electronic configuration of the oxygen atom and the pairing of electron spins from each atomic orbital involved in the bonding is shown below.



Two oxygen atoms share two electron pairs, *i.e.*, they are joined by double bond ($=$). Both the electron pairs are expected to be spin paired. The scheme of the formation of oxygen molecule shows that each oxygen atom has two p orbitals which are singly filled. When

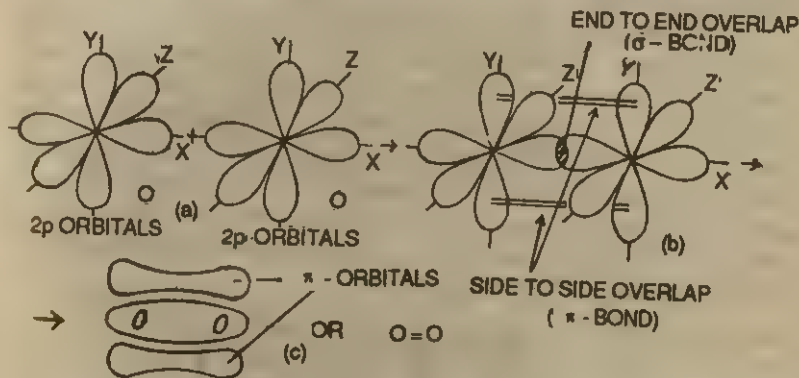


Fig. 6.38 Oxygen molecule : (a) two separate p orbitals, (b) overlapping of two p orbitals, bond is formed by the end to end overlap of $p_x - p_x$ orbitals; bond is formed by side-to-side overlap of $p_y - p_y$ orbitals, and (c) sigma and pi bonds orbitals.

two oxygen atoms approach each other two electrons from each atom pass into a bonding region between the two nuclei. Because of the Pauli's exclusion principle, two orbitals are required for these four electrons. One bonding orbital is formed along with X-axis when two

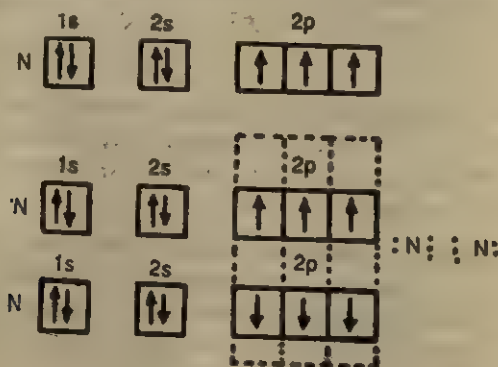
half-filled $2p_x$ orbitals overlap. This results in the formation of a single covalent σ bond. Now that the two oxygen atoms have been drawn close, another bonding orbital is formed as a result of side to side overlap of the two half-filled $2p_y$ orbitals. This bonding orbital is split into two regions. The upper and lower overlaps, taken together, constitute a new type of single covalent bond, the π bond.

On rotation of the oxygen atoms, the P_y orbitals are quickly twisted out of overlap, and therefore, such rotation is prohibited for a sideways overlap. Another important property of the π bond arises from the fact that the electrons (charge cloud) are placed above and below the plane of the bonding atoms. Hence, these electrons are more susceptible to attack especially by the electron seeking (oxidizing) reagents. Under the circumstances π bond is stronger than σ bond.

Experiments have shown that O_2 is paramagnetic in nature, i.e., it is attracted by a magnetic field particularly when in solid or liquid state. Nitrogen has been found to be diamagnetic. The paramagnetism of O_2 indicates that the diatomic molecule contains two unpaired electrons (i.e., two electrons have the same spins). Our simple picture of oxygen molecule has, thus, failed to predict its paramagnetic behaviour. This can be well explained on the basis of molecular orbital theory which will be taken up later in class XII.

Nitrogen Molecule, N_2

A nitrogen molecule is formed by the union of two atoms. Bonding could be envisaged when two $2p_x$ orbitals approach linearly and overlap forming σ bond. The other two pairs of orbitals, i.e. $2p_y$ and $2p_z$ orbitals overlap laterally forming two π bonds (Fig. 6.39) and the two lone pair of electrons would occupy the two $2s$ orbitals present in the nitrogen atoms. Again the formation of a stable bonds due to the overlap of electron clouds can be illustrated schematically in terms of the pairing of electron spins from each atomic orbital involved in the bond formation, as shown below for N_2 .



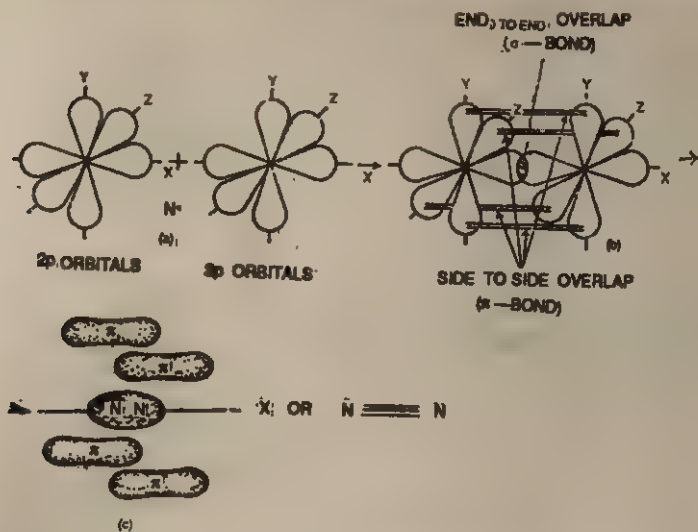


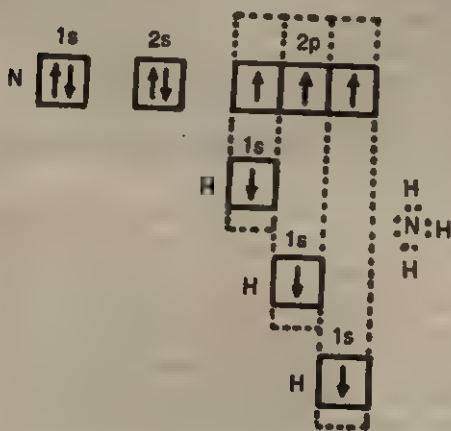
Fig. 6.39 Nitrogen molecule; one pair of orbitals overlap end to end to give σ bond; the other two pair of orbitals overlap sideways to give π bonds.

Three electron pairs are shared resulting in a triple bond in the molecule. This structure would give each nitrogen atom a completed octet of electrons in its outershell and would show that all the electrons are spin paired.

Ammonia Molecule, NH_3

The electronic configuration of nitrogen includes one electron in each of the three 2p orbitals. Bonding could, thus, be understood by allowing σ bonds to be

formed from the overlapping of a hydrogen 1s orbital with each of the nitrogen singly occupied 2p orbitals and the lone pair of electrons would occupy the 2s orbital (Fig. 6.40). The formation of a stable bond due to the formation of electron clouds can be portrayed schematically in terms of pairing of electron spins from each



atomic orbital involved in the bonding as shown above for NH_3 .

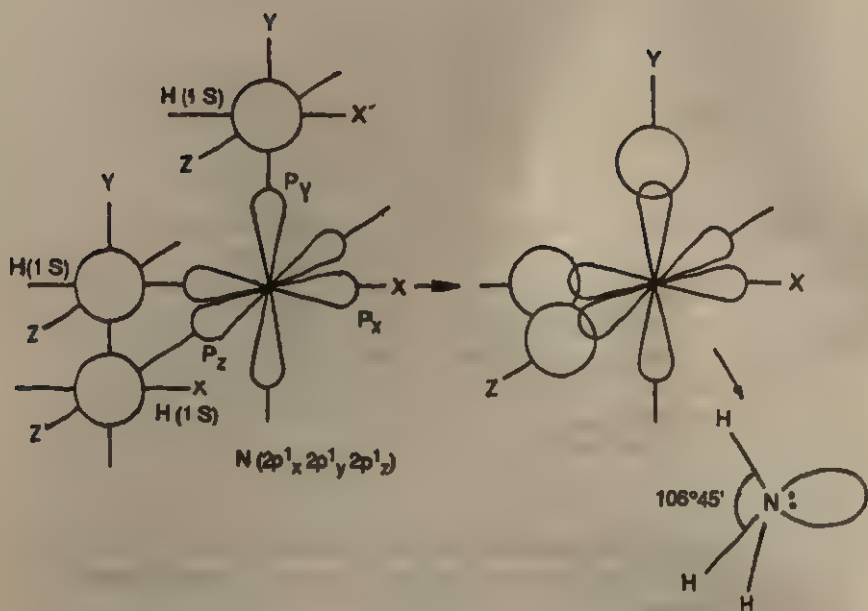


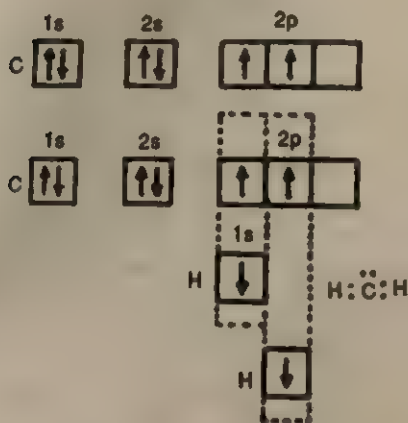
Fig. 6.40 Bond formation in NH_3 using pure s and p orbitals

The fact that the three $2p$ orbitals point in three different directions at right angles to one another accounts clearly for the bent pyramidal geometry of NH_3 , with three hydrogen atoms forming a base and the nitrogen atom at the apex. In this model, all H-N-H bond angles should be 90° . The experimentally measured bond angles are actually somewhat larger than 90° , (i.e., $106^\circ 45'$) but we can explain this enlargement of bond angle by allowing that there must be repulsive forces between the hydrogen atoms, which will carry partial positive charge as a consequence of being bound to the very electronegative N atom.

6.5 THE CONCEPT OF HYBRID ORBITALS AND GEOMETRY OF MOLECULES

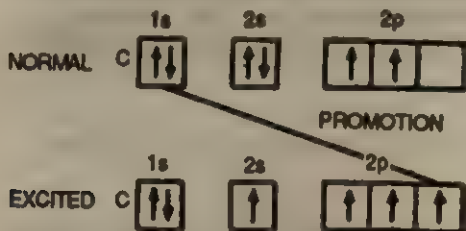
The valence bond theory of the covalent bond considers the bond to be the result of the overlap of two atomic orbitals, each containing an unpaired electron. This theory cannot be used to account for all molecular structures. It explains the formation of covalent bonds in simple molecules like H_2 , HF , etc. The treatment given to H_2O and NH_3 is not fully adequate as the description of bonding in H_2O and NH_3 molecules does not agree with structural parameters for the molecules. The simple valence bond approach to covalent bonding also met with failure as it could not explain the number of bonds present in the simple molecules such as BeCl_2 , BF_3 , and CH_4 .

A consideration of the electronic configurations of beryllium ($1s^2, 2s^2$), boron ($1s^2, 2s^2, 2p^1$) and carbon ($1s^2, 2s^2, 2p^2$) suggests that these elements should be zerovalent, monovalent and bivalent respectively. But actually this is not true. The elements are, however, typically bivalent, trivalent and tetravalent respectively. As a result, two half-filled $2p$ orbitals in carbon would be expected to overlap with $1s$ orbitals of two hydrogen atoms to form CH_2 as illustrated below :



However, CH_2 is not a stable molecule. Even if it could be produced, it is highly reactive. This is because, CH_2 molecule is electron deficient, i.e., carbon atom has only a sextet (i.e., six) of electrons rather than stable octet electron structure. Although, there are an enormous number of carbon compounds ; the problem of instability hardly exists. Carbon, in all these compounds, is tetravalent.

The simplest stable molecule formed between carbon and hydrogen is the familiar methane molecule. Thus, carbon atoms form four σ bonds. The molecule is a regular tetrahedron with a C atom at the centre, H atoms at the four corners, and $\text{H}-\text{C}-\text{H}$ bond angles of $109^\circ 28'$ each. In terms of atomic orbitals, this requirement can be met by uncoupling one of the $2s$ electrons and promote it to $2p$ level (this process would require energy). This process is called promotion.



Four singly occupied orbitals. All can participate in bond formation to form tetravalent carbon compound.

The molecular geometry predicted from the orbital diagram would be molecule with three C-H bonds at 90° and the fourth, undirected. Thus, the orbital diagram accounts for the correct number of C—H bonds but not the spatial orientation of these bonds. Since the formation of bonds involves fall in energy, the formation of four

bonds would experience a drop in energy more than that of two bonds (by a divalent carbon atom). This additional lowering of energy more than compensates for the energy required to uncouple and then promote the 2s electron to the higher energy 2p orbital. In fact, the energetics of the process explain why CH_4 is the stable molecule rather than CH_2 (Fig. 6.41).

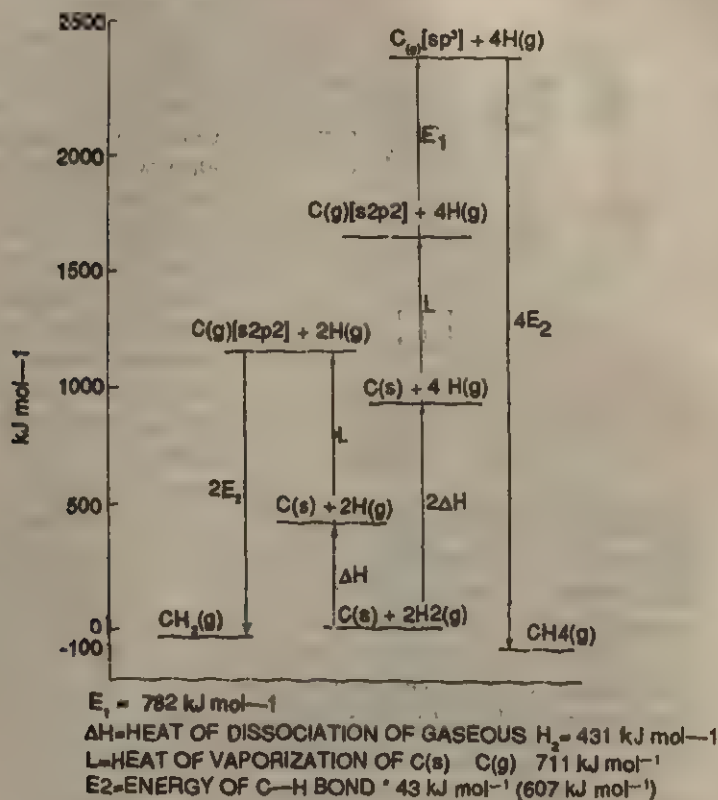
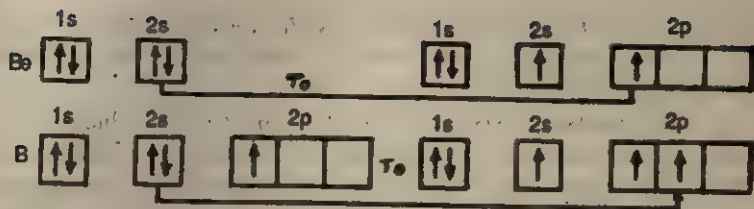


Fig. 6.41 Energy changes involved in the formation of CH_2 and CH_4

Similarly acceptable Lewis structures for BeCl_2 and BF_3 require two and three unpaired electrons respectively. In terms of atomic orbitals the requirement can be fulfilled by promoting electron from 2s to 2p level. The promotion scheme for the two elements is :



Promotion leads to an overall drop in energy because it increases the bonding capability of Be and B.

Hybridization Of Orbitals

The number of unpaired electrons in the excited states corresponds with the observed combining power of the atoms: However, such a state does not explain the fact that all bonds are equivalent in a molecule such as BeCl_2 , BF_3 , BCl_3 , CH_4 or CCl_4 . To overcome this, the concept of hybridization of atomic orbitals is introduced. It involves the mixing up of atomic orbitals to produce composite orbitals (orbitals of equivalent energy) that we call hybrids. Atomic orbitals involved in hybridization are nearly of same energy. At this stage, it must be made absolutely clear that this is not a phenomenon, i.e., it is not a process which we can observe and study. It is essentially a mathematical convenience - a system of rearranging the electrons associated with atomic orbitals such as to reconcile them with the observed shapes of molecules.

The concept of hybrid orbitals can be extended to explain the bonding about any central atom. In such explanations the following facts apply :

1. The number of hybrid orbitals is equal to the number of ground state orbitals.
2. Hybrid orbitals of the same type are equivalent in energy with maximum symmetry.
3. Hybrid orbitals always have a greater tendency for overlapping than do the atomic orbitals.
4. Hybrid orbitals have definite orientation in space and point in direction that are consistent with the observed shape of the molecule and are used to construct bond orbitals.

Geometry Of Molecules

The use of the pure atomic s and p orbitals has failed to account for the shapes of most of the molecules. The description of simple atomic orbital (s, p, d, etc.) is based on isolated atoms. The electronic arrangements for the isolated atoms are not applicable to bonded atoms. They have been successful in explaining some covalent bonds.

The linear, trigonal, and tetrahedral shapes for various molecules cannot be explained by using simple atomic orbitals and the idea of hybrid orbitals had to be introduced.

Covalent bonds have direction. In a molecule in which two or more covalent bonds are present, molecular geometry is dictated by the bond angles about the central atom. The nonbonding electrons also affect the molecular geometry.

sp^3 Hybridization

The mixing up of one s and three p orbitals produces four sp^3 (pronounced espsee three) hybrid orbitals that are directed towards the four corners of a regular tetrahedron making an angle of $109^\circ 28'$ with each other (Fig. 6.42). The sp^3 hybridization scheme is suggested below through orbital diagrams.

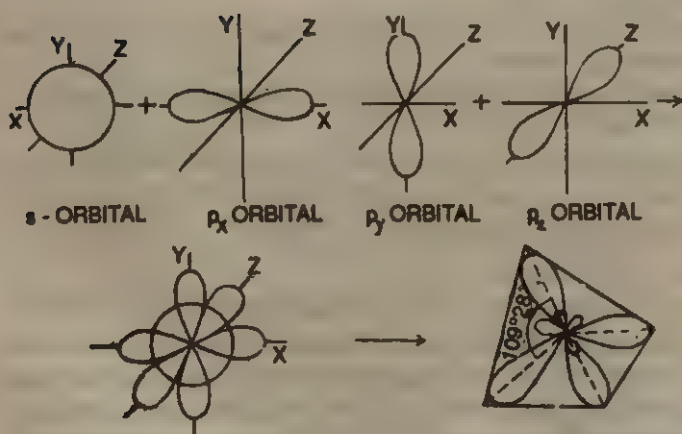
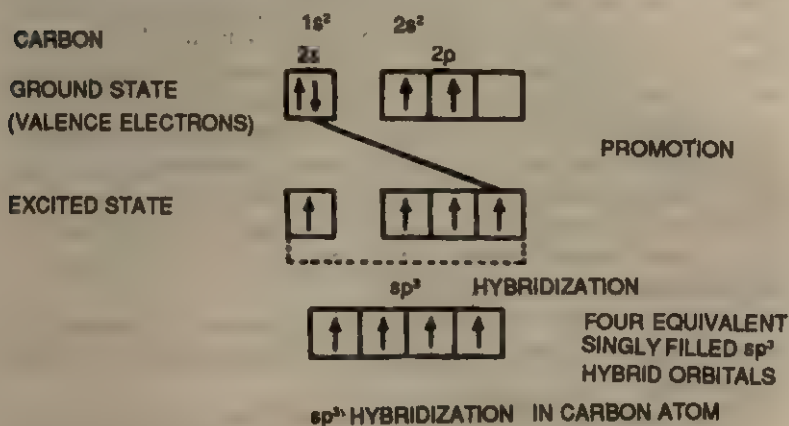


Fig. 6.42 Process of tetrahedral hybridization - one s and three p orbitals on mixing form four sp^3 hybrid orbitals of equivalent energy.

Methane : In the formation of methane (CH_4), the singly occupied $1s$ orbital of each of the four hydrogen atoms overlaps with the four singly filled sp^3 hybrid orbitals of the carbon atom (Fig. 6.43) forming four C-H σ bonds. This results in a regular tetrahedral distribution of σ bonds.

Ethane : In ethane, the carbon orbitals are sp^3 hybridized and bonding occurs by overlap of one hybrid orbital of one of the carbon atoms with the hybrid orbital of the other carbon atom to form a bond between two carbon atoms. The remaining three hybrid orbitals on each carbon atom overlap with six $1s$ atomic orbitals on six hydrogen atoms to form six C-H σ bonds (Fig. 6.44). The structures of other saturated hydrocarbons or their derivatives (CH_3F , $CHCl_3$, CH_2Cl_4 , C_2H_5Cl , etc.) may be arrived at in the same fashion.

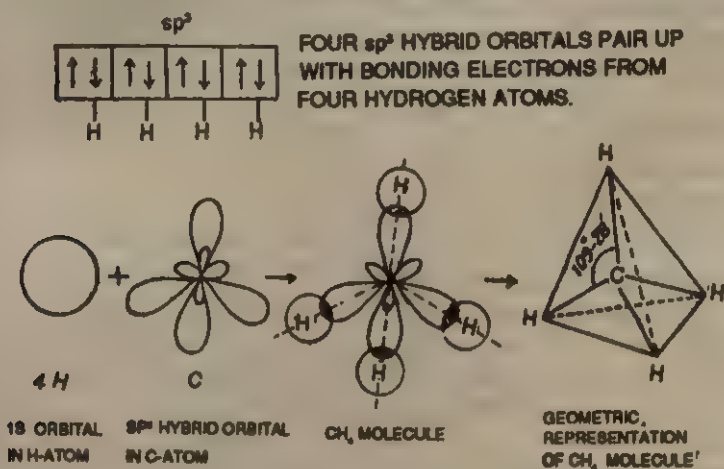


Fig. 6.43 Formation of tetrahedral methane molecule by overlap of carbon sp^3 hybrid orbitals with $1s$ atomic orbitals of hydrogen

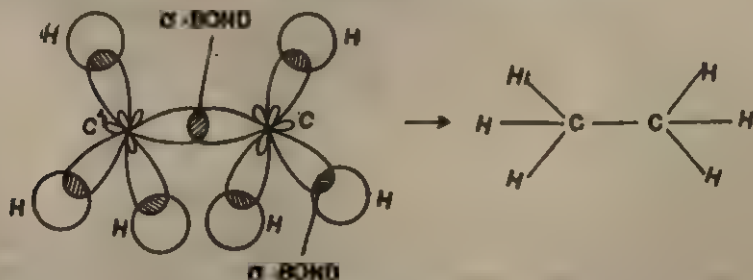


Fig. 6.44 Formation of ethane molecule; orbital diagram

Ammonia : Even in cases where the number of bonds to be formed in a molecule is fewer than the number of pairs of electrons available, it is possible to explain the observed bond angles in terms of hybridization. For example, it can be assumed that in the ammonia, NH_3 molecule, the nitrogen atom uses four sp^3 hybrid orbitals to accommodate the four electron pairs. Three of these hybrid orbitals overlap with $1s$ orbitals from the three different hydrogen atoms forming N-H bonds and the fourth orbital contains the unshared electron pair. On the basis of s-p overlapping model the $\text{H}-\text{N}-\text{H}$ bond angle should be 90° , and in the model invoking sp^3 hybridization it should be $109^\circ 28'$ (Fig. 6.45). The experimentally observed angle is $106^\circ 45'$ which shows that the actual structure is between these two extreme models, implying that the degree of hybridization in the NH_3 molecule is less than in methane. The hybridized model of NH_3 has a triangular pyramidal shape. The scheme of formation of the NH_3 molecule is given below :

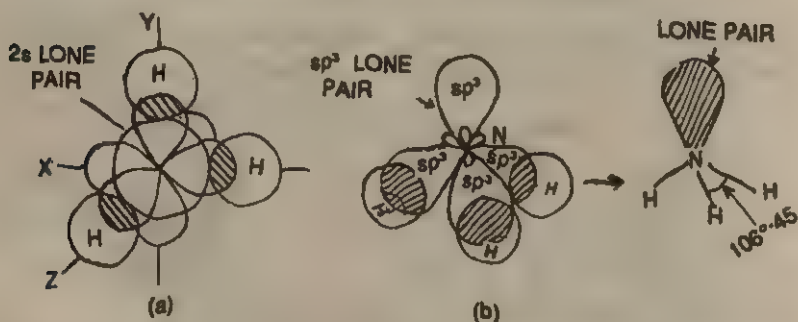
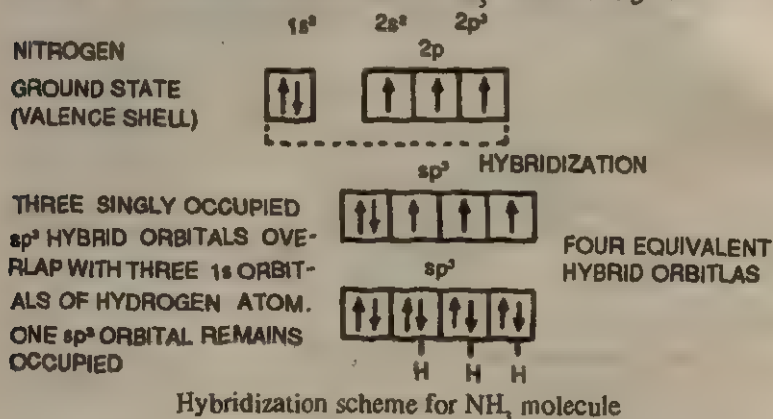


Fig. 6.45 Two extreme models of ammonia molecule: (a) bond formation in NH_3 using pure s and p orbitals, (b) bonding in NH_3 using sp^3 orbitals of nitrogen

The scheme of formation of NH_3 molecule shows that three of the orbitals about the nitrogen atom are the intermediate of hybrid sp^3

and pure p in character, and the unused fourth orbital is between hybrid sp^3 and pure s. The lone pair of electrons occupies this latter orbital.

The structures of PF_3 , PCl_3 , NCI_3 , PH_3 , etc. can be arrived at in same way.

WATER : The description of the water, H_2O molecule in terms of hybrid orbitals is very similar to that of NH_3 . Two sp^3 orbitals overlap with 1s orbitals from the two hydrogen atoms forming O-H bonds to give the molecule a bent shape while the other two orbitals hold unshared electron pairs (Fig. 6.46). The bond angle $H-\hat{O}-H$ is $104^\circ 27'$ which indicates that the degree of hybridization is less than that of NH_3 . The plausible scheme of the formation of water molecule is suggested below through orbital diagram :

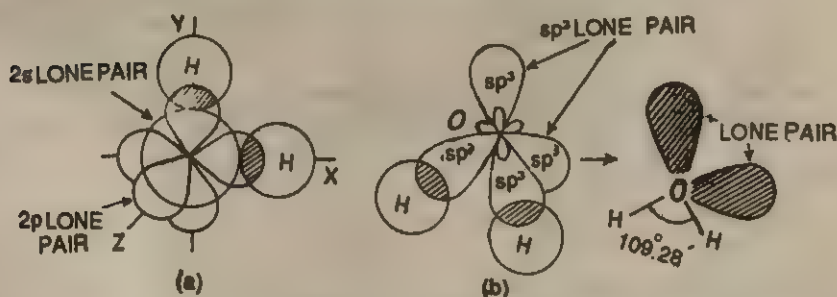
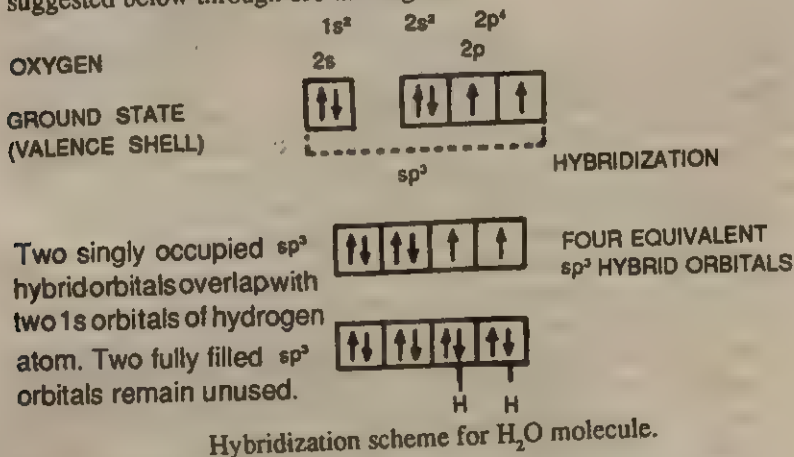


Fig. 6.46 Two extreme models of the water molecule: (a) bond formation in H_2O using pure s and p orbitals, (b) bonding in H_2O using sp^3 orbitals of oxygen

Thus, the structures of H_2S , H_2Se , H_2Te , etc. are all V - shaped as required by the electron structure of oxygen atom.

sp² Hybridization

The mixing of one s and two p orbitals produces three sp² hybrid orbitals of equivalent energy. These orbitals are directed towards three corners of an equilateral triangle at an angle of 120° to each other in a plane (Fig. 6.47). The unused third p orbital takes part in bond formation in its original form.

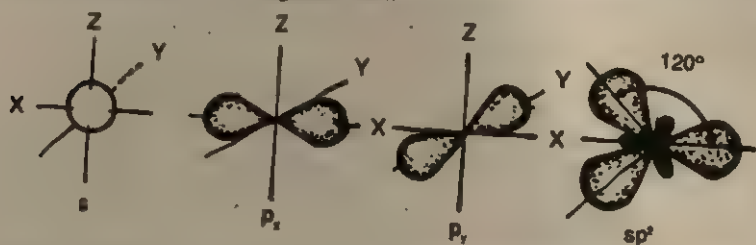
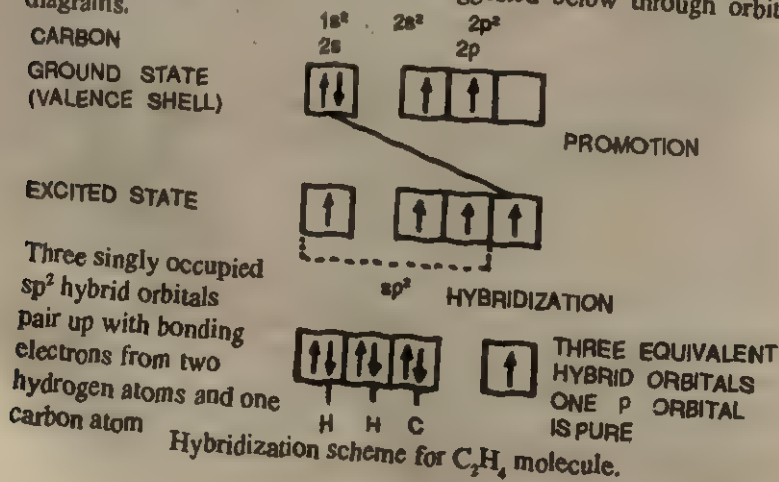


Fig. 6.47 Process of trigonal hybridization - one s and two p orbitals on mixing form three sp² hybrid orbitals.

Ethene: The bonding in ethene (or ethylene, an unsaturated hydrocarbon) is usually interpreted in terms of sp² hybridization. Two of the sp² hybrid orbitals from each carbon atom form the four σ type C-H bonds by overlapping with the four 1s orbitals of four hydrogen atoms. Overlap of the remaining two sp² hybrid orbitals, one from each carbon atom gives rise to σ bond between the two carbon atoms. Each carbon has also one electron located in a pure 2p orbital, the axis of which is perpendicular to the plane of the hybrid orbitals. These 2p orbitals add to the stability of the molecule by overlapping sideways to form a second π type C-C bond (Fig. 6.48). The electron cloud is concentrated above and below the C-C axis.

The hybridization scheme in the bonding of hydrogen and carbon in the formation of ethene is suggested below through orbital diagrams.



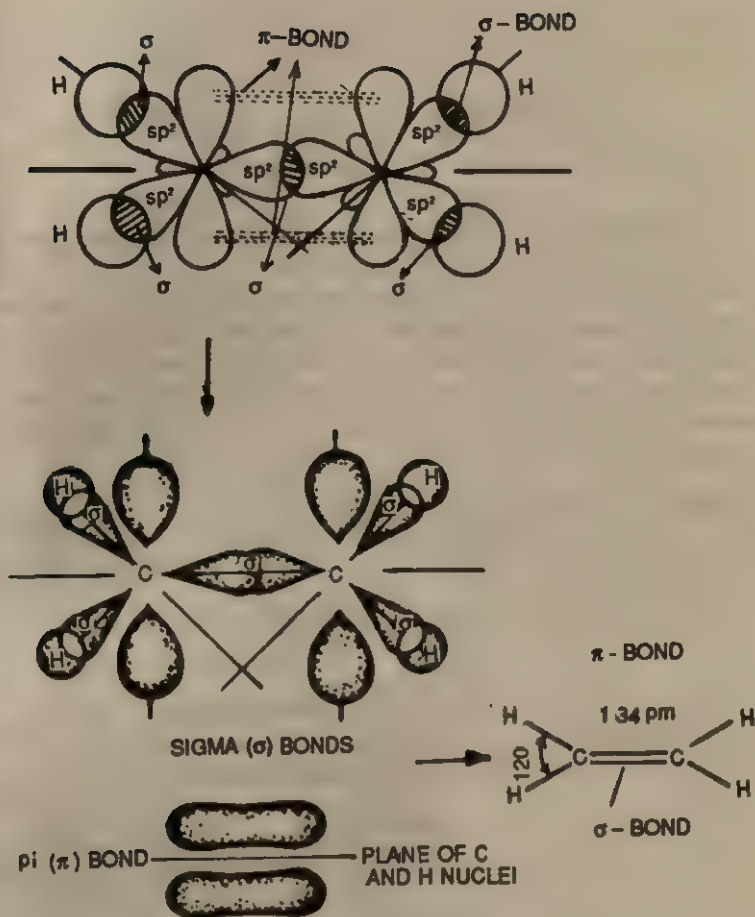
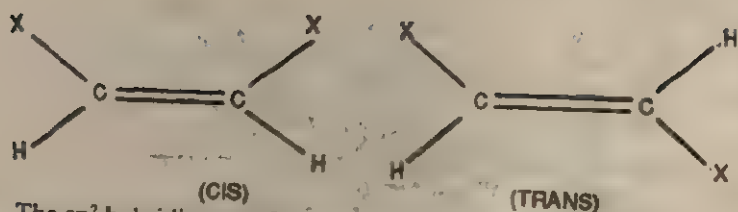


Fig. 6.48 Formation of ethylene molecule.

Sideways overlap is maximum when the C-H bonds are all coplanar. The degree of overlap of the two pure $2p$ atomic orbitals is less than the overlap of the two sp^2 hybrid orbitals. This difference in overlap makes the π bond weaker than σ bond. The weak nature of π bond attributes to the reactivity of ethylene. The two carbon atoms tend to form a more stable σ bond with other atoms. The presence of π bond (in addition to σ bond) suggests that the two carbon atoms are bound more strongly than by a single σ bond. This results in decreasing the bond length. The CH_2 fragments in ethene cannot be rotated with respect to each other as on rotation the $2p$ orbitals are quickly twisted out of overlap. This prohibited rotation accounts that the disubstituted ethene molecules can exist as two geometric isomers, viz., the cis and trans.

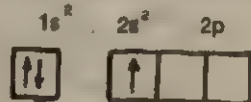


The sp^2 hybridization also accounts for the bonding and shape of molecules such as BX_3 ($X = F, Cl, Br$ or I).

Boron Trihalides : In BF_3 , B uses three sp^2 hybrid orbitals which are occupied by each of the three unpaired electrons. Each B-F bond results from the overlapping of one sp^2 hybrid orbital with a fluorine 2p orbital containing an unpaired electron (Fig. 6.49). The hybridization scheme in the bonding of boron and fluorine for BF_3 molecule is suggested below :

BORON

GROUND STATE
(VALENCE SHELL)



PROMOTION



EXCITED STATE

sp^2 HYBRIDIZATION



THREE EQUIVALENT SINGLY
FILLED sp^2 HYBRID ORBITALS



PAIR UP WITH BONDING
ELECTRONS FROM THREE
FLUORINE ATOMS

Hybridization scheme for BF_3 molecule

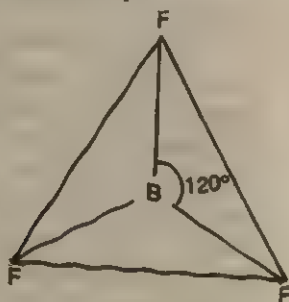
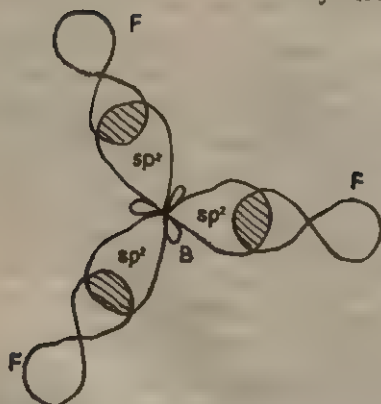


Fig. 6.49 Formation of trigonal BF_3 molecule by overlap of boron sp^2 hybrid orbitals with 2p orbitals of fluorine.

Thus, the structure of BCl_3 , BBr_3 , BI_3 , etc. are all trigonal as required by the electron structure of the boron atom.

sp Hybridization

This is the simplest case of diagonal hybridization, where two orbitals, i.e., one s and one p orbitals on moving together form two sp hybrid orbitals (Fig. 6.50). The two sp hybrid orbitals are directed along a straight line, at a 180° angle. The unused two p orbitals take part in bond formation as pure p orbitals.

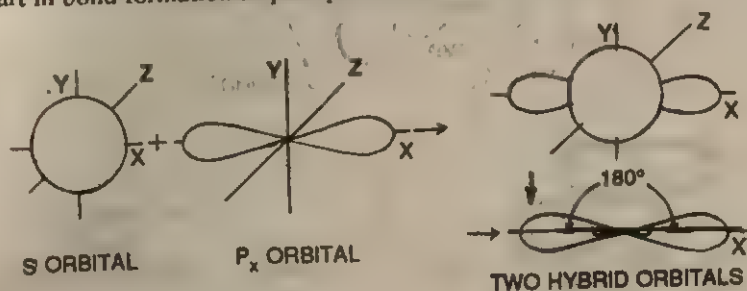
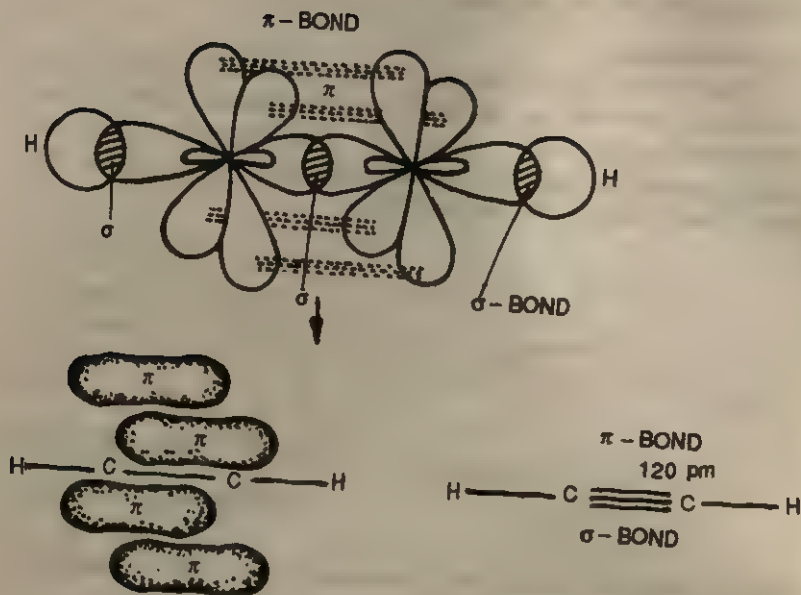


Fig. 6.50 Process of diagonal hybridization - one s and p orbitals on mixing form two sp hybrid orbitals.

Ethyne : In the ethyne (C_2H_2) molecule, each carbon is attached to other atoms, a hydrogen and a carbon atom. Two orbitals are required around each carbon atom for the purpose. The bonding scheme involves sp hybrid orbitals.

In ethyne (acetylene) one 2s and one 2p orbitals on each carbon atom hybridize to form sp hybrid orbitals. This leaves on each carbon atom two singly occupied unhybridized 2p orbitals that are mutually perpendicular to the sp hybrid orbitals. One sp hybrid orbital on one carbon atom overlaps with that of the other forming a σ bond. The remaining sp hybrid orbital on each carbon atom overlaps with the 1s atomic orbital of hydrogen to form C-H bonds. Two π bonds are also formed by the overlap of the unhybridized two 2p orbitals (Fig. 6.51) on each carbon atom. Thus, acetylene molecule will consist of a triple bond constituted of one σ and two π bonds.

Further, it is important to note that in compounds having multiple bonds, one bond would be σ bond the other would be π bonds. For example, in oxygen molecule, as we have seen earlier, there is one σ and one π bond, in nitrogen there is one σ and two π bonds in



FORMATION OF π BONDS

Fig. 6.51 Formation of ethyne molecule

ethylene, there is one σ and one π bond.

Beryllium Fluoride: The structure of BeF_2 is also explained on the basis of sp hybridization. In the molecule, Be atom with two sp hybrid orbitals overlaps with the two half-filled fluorine $2p$ orbitals as shown in Fig. 6.52. The structures of BeCl_2 , BeBr_2 , CO_2 , CS_2 , etc. are all linear as required by the electron structure of the beryllium atom.

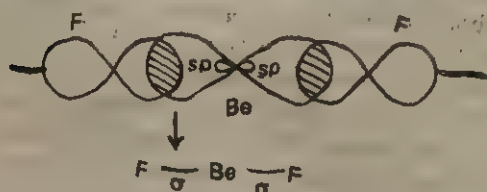
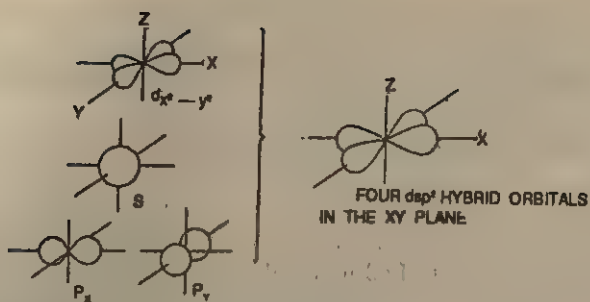


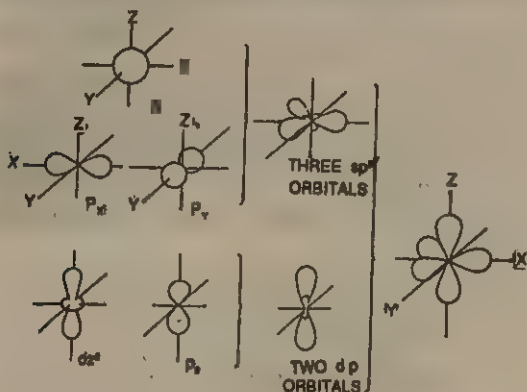
Fig. 6.52 Overlapping of p orbitals of fluorine atoms with sp hybrid orbitals of Be in BeF_2

In many compounds d orbitals are also involved and can give rise to more complicated hybrid orbitals, e.g., dsp^2 , sp^3d and sp^3d^2 (Fig. 6.53). The involvement of d orbitals

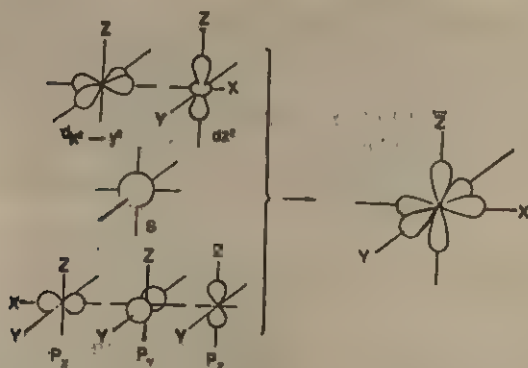
starts from third period elements. Both phosphorus and sulphur are from third period. Their electronic arrangements for the valence shell are $3s^2 3p^3$ and $3s^2 3p^4$ respectively. They form compounds like PF_3 , PF_5 , H_2S , SF_4 , SF_6 , etc. The structures of PF_3 and H_2S can be explained by sp^3 hybridization scheme (seen in NH_3 and H_2O). In explaining the stereochemistry of PF_3 , SF_4 and SF_6 vacant d orbitals are



(a) Mixing of Orbitals to give four Equivalent dsp^2 Hybrid Orbitals



(b) Mixing of Orbitals to give five dsp^3 or sp^3d Hybrid Orbitals



(c) Mixing Orbitals to give six Octahedrally disposed d^2sp^3 or sp^3d^2 Hybrid Orbitals

Fig. 6.53 Mixing of orbitals to give dsp^2 , sp^3d , and sp^3d^2 Hybrid Orbitals

sity is distributed equally over the two atoms. An extreme example would be a chemical bond between two identical atoms, as in H_2 , F_2 , etc. With the positive and negative charges equally distributed, the H_2 and F_2 molecules are non-polar.

When two atoms of very different electronegativity are joined together, the bonding electrons tend to be drawn close to the more electronegative atom. In CsF , the electrons in the bond spend virtually all their time close to fluorine (highly electronegative). Under the circumstances, it is justified to say that an electron has been transferred from the caesium atom to the fluorine atom, which therefore, behaves as a negative ion (F^-), while the less electronegative Cs becomes a positive ion (Cs^+). These ions are attracted to one another by their opposite charges. As a result, an ion pair Cs^+F^- is formed. This is an extreme example of polar covalent bonds.

Between the extremes of purely covalent and purely ionic bonding there can be found examples of all kinds of intermediate polarity. It is possible to estimate the percentage of ionic nature of a polar covalent bond from experimental data. Dipole moment data can provide valuable information about the manner in which electrons are shared between bonded atoms.

It is important to know that the bonds in molecules are always of the polar covalent type, since 100% covalent or ionic bonds are not possible. However, a polar covalent bond which is mostly ionic (*i.e.*, with $> 50\%$ ionic in character) is generally called ionic. Similarly, the one with a mostly covalent character (*i.e.*, $< 50\%$ ionic in character) is mostly known as covalent.

6.7 IONIC CHARACTER OF BONDS AND POLAR MOLECULES

6.8.1 Molecular Polarity and Dipole Moments

Ionic and non-polar covalent bonds represent extremes in chemical bonding. As ionic bond is formed because of the electrostatic attraction between two oppositely charged ions and is, thus, expected to be a polar bond. On the other hand, in the non-polar covalent bonds electrons are shared equally between like atoms, and charge distribution is uniform. There is absolutely no ionic character.

When a covalent bond joins atoms of two different elements, the shared pair of electrons is not shared equally. The result of this unequal attraction for electrons is that the electrons are pulled closer to the atoms of one element than the other. For example, in case of hydrogen chloride molecule, chlorine atom has more affinity for electrons than hydrogen atom. Therefore, the pair of electrons is held close to the chlorine atom. This means that the H end of the HCl molecule is slightly positive (usually indicated by δ^+) and the Cl end is slightly negative (δ^-). This is illustrated in Fig. 6.54.

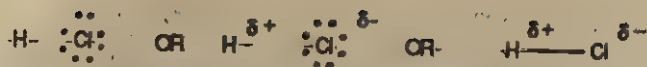
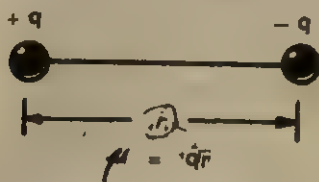


Fig. 6.54 The hydrogen chloride molecule the covalent bond is polar

Such covalent bonds formed between dissimilar atoms are polar covalent bonds and such molecules are called polar molecules. A pair of two separated, equal and opposite charges is called a **dipole**. A dipole is described quantitatively by its dipole moment, μ which is defined as the product of the magnitude of the charge q at each end of the dipole and the distance r between the charges. According to SI



units q is measured in coulombs and the distance r is measured in metres. So it will be measured in coulombs metres, Cm.

Definition of the dipole moment
The dipole moment of a molecule is the resultant of the individual bond dipoles. Each bond-dipole is described by a vector designated by an arrow that points from the positive to the negative end. Therefore, the resultant dipole moment of the molecule is equal to bond dipole vector addition as illustrated in Fig. 6.55.

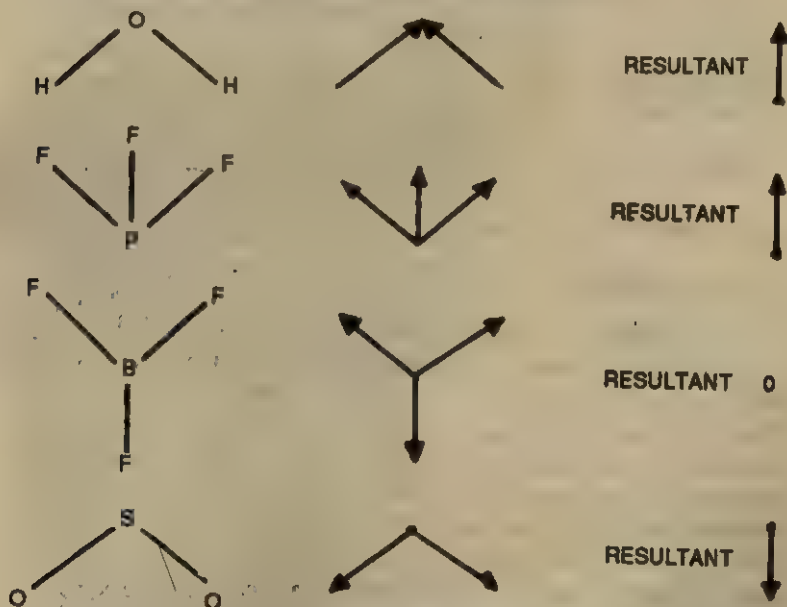


Fig. 6.55 Bond dipole vector addition. The arrow (\longrightarrow) points from + to - end of the polar bond. The resultant vector is the final dipole of the molecule

A molecule that has a dipole moment is called a polar molecule. Since it has two poles, it is also called a dipolar molecule. All diatomic molecules with polar covalent bonds have dipole moments, and thus, are polar. But not all polyatomic molecules with polar covalent bonds are polar. The effect of individual polar bonds on the polarity of an entire molecule depends on the shape of the molecule and the orientation of the polar bonds about the central atom. So in polyatomic molecules, the dipole concept is applicable to an individual bond. Not all molecules with charge centres are polar. A molecule is polar only if charge centres are unsymmetrical. Even if the individual bonds within a molecule are polar, the molecule as a whole can be non-polar if the charge distribution is symmetrical, i.e., the centre of all the negative charges and the centre of all the positive charges coincide, e.g. CCl_4 and BF_3 have zero net dipole moment.

Carbon dioxide : Carbon dioxide, for example, is a linear molecule with partial negative charges around the more electronegative oxygen atoms. This is balanced by partial positive charges around carbon as illustrated in Fig. 6.56. In CO_2 , the centre of two negative charges on oxygen atoms coincide with the centre of positively charged carbon atom, so the molecule has no dipole moment.

Although the individual bonds are polar, the polarity of one bond cancels the polarity of the other because of the symmetry in charge distribution. This makes the molecule non-polar. The total dipole moment of a molecule is the sum of the individual bond dipoles within the molecule, which add together like vectors. In CO_2 molecules, these bond dipoles are oriented in opposite directions and they effectively cancel each other. Hence the net dipole moment is zero.

Beryllium fluoride : It has two polar covalent bonds and is linear. Its net molecular dipole moment is zero. (Fig. 6.57). The beryllium and fluorine atoms lie along the same axis, therefore, the bond polarities cancel because they are in opposite directions.

Water: The triatomic H_2O molecule has a dipole moment ($\mu = 1.85 \text{ D}$; Deby (D) $= 3.34 \times 10^{-30} \text{ Cm}$). This fact immediately rules out the

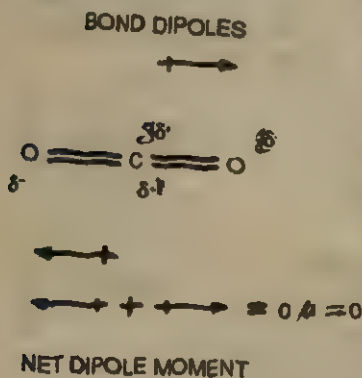


Fig. 6.56 Carbon dioxide molecule. Centre of positive and negative charges coincide i.e., there is no charge separation between the centres of positive and negative charges. An arrow with a plus(+) sign on one end is used to represent the bond dipole

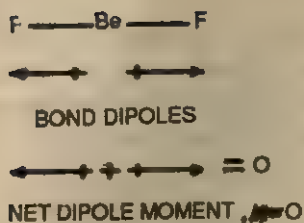


Fig. 6.57 Dipole moment diagram of BeF_2 (a non-polar molecule)

linear structure for H_2O and supports its angular structure. The dipole moment value is in agreement with the angular structure predicted for a molecule with four electron pairs about the central atom. In water molecule, the centre of the positive charges is situated near the hydrogen atoms, so there is a charge separation and a dipole moment (Fig 6.58). The net molecular dipole (\longrightarrow) is drawn to show this separation of

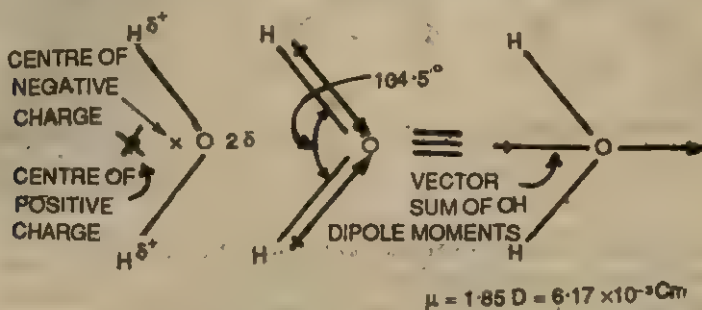


Fig. 6.58 Dipole moment diagram of H_2O molecule (a polar molecule)

charges arising from the two or individual bond dipoles. The asymmetry (geometrical imbalance) of the polar bond distribution leads to separation of the centres of charges - a necessary condition for any molecule that has dipole moment. Molecules with dipole moment are described as polar molecules.

Sulphur dioxide : Sulphur dioxide illustrates the effect of molecular shape on dipole moment. We expect $\text{S} - \text{O}$ bond to be polar. Sulphur dioxide molecule has a dipole moment of $5.42 \times 10^{-30} \text{ Cm}$. This is because of the angular structure associated with SO_2 molecule. The two $\text{S} - \text{O}$ dipoles make an angle of 120° to each other, and hence,

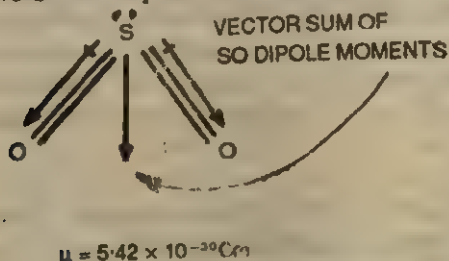


Fig. 6.59 Prediction of angular shape for SO_2 from the measurement of dipole moment

they do not cancel each other; their vector sum gives a net molecular dipole (or resultant dipole) pointing along the bisector of $\text{O} - \text{S} - \text{O}$ angle (Fig. 6.59). Thus, for a tri-atomic molecule with central atom (A) and other two identical atoms (B),

the measurement of dipole moment can convey to us whether the molecule is linear or angular.

Boron trifluoride : Boron trifluoride illustrates the effect of its molecular shape on dipole moment. It has a trigonal shape. Its highly polar bonds (electronegativity difference, $\Delta EN = 2.1$) are inclined at 120° . Its shape causes the centres of negative charges on the F atoms and positive charge on the B atom to coincide (Fig. 6.60). Therefore,

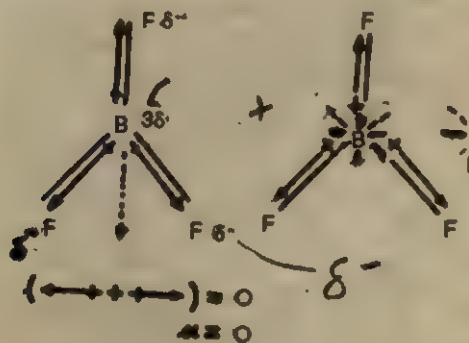


Fig. 6.60 Dipole moment diagram of BF_3 . Superimposed + and x marks the spot where the centres of positive and negative charges coincide

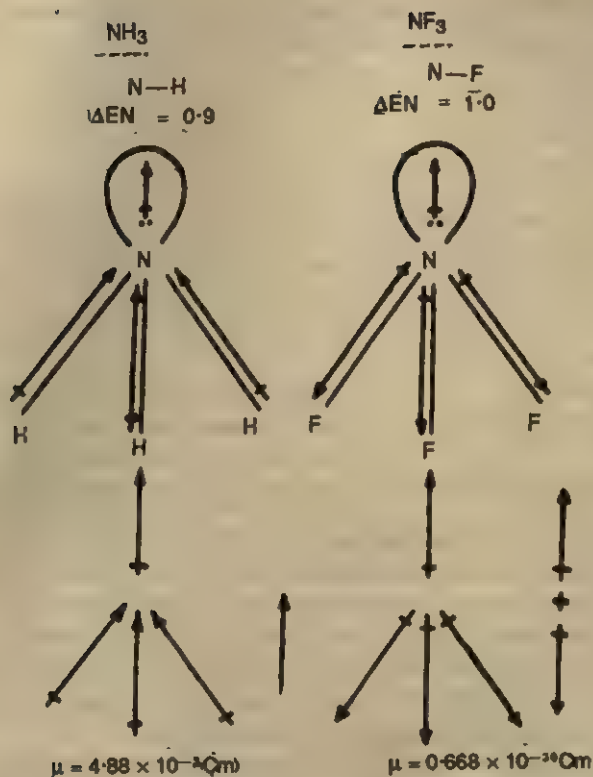
the molecule has no dipole moment. In other words, BF bond dipoles present in symmetrical planar trigonal arrangement have a vector sum of dipole moment zero by the law of parallelogram of forces. It supports the presence of three fluorine atoms at the vertices of an equilateral triangle with the boron at the centre. Therefore

BF_3 is a non-polar molecule. The lack of polarity in the molecule is predicted from its low b.p. (172 K). Other molecules such as BCl_3 , BI_3 , BBr_3 , and SO_3 have also zero dipole moment.

Phosphorus trichloride : Its trigonal structure with a lone pair of electrons (triangular pyramidal shape) has a dipole moment ($\mu = 2.30 \times 10^{-30}$ Cm). Molecules that have one or more non-bonding electron pairs in the valence shell of the central atom have a dipole moment (except linear AX_2E_3 and square planar AX_4E_2 structures, where E = number of nonbonding electron pairs) whereas others that do not have a non-bonding electron pairs have no dipole moment. Molecules similar to PCl_3 , such as PF_3 , PBr_3 , NH_3 , NF_3 , etc. have dipole moment. In NH_3 and NF_3 , the electronegativity differences are nearly equal but the resulting nearly equal bond polarities are in opposite directions. Each of them has one lone pair of electrons of which contribution towards polarity is shown in Fig. 6.61.

Tetrahedral molecules

The tetrahedral structures of carbon compounds of the general formula CX_4 have bonds of various polarities distributed equidistantly about the central atom. In these structures, the bond dipoles point



Bond dipoles reinforce the effect of the lone pair of electrons. Therefore, NH₃ is highly polar.

Bond dipoles oppose the effect of lone pair of electrons. Therefore NF₃ is slightly polar.

Fig. 6.61 A comparison of dipole moments in NH₃ and NF₃

toward the corners of tetrahedron. For example, in methane, carbon is more electronegative than H (EN for H = 2.1; EN for C 2.5). This means that the pair of bonding electrons will be closer to the carbon atom. Each of the four C-H bonds will be the same. As a result, the carbon atom will be the centre of negative charge and that each of the hydrogens will form a region of equally strong positive charge. Further a molecule where there is symmetrical distribution of polar bonds, the centres of positive and negative charge coincide, therefore, the molecule has no dipole moment and is nonpolar.

A similar conclusion can be arrived at if we consider the bond dipoles, i.e., a tetrahedron arrangement leads to complete cancellation of the dipoles. Each individual bond dipole is cancelled by the effects of the other three that point particularly in the opposite direction.

Therefore, tetrahedral molecules such as CCl_4 , CF_4 , CH_4 , etc. are non-polar, even though they have polar bonds.

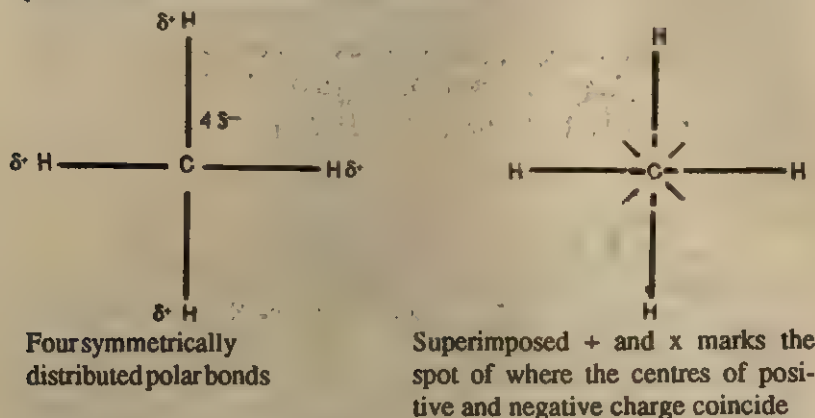


Fig. 6.62 Dipole moment diagram of the non-polar methane molecule

Exercise 6.3 : Is the chloroform molecule CHCl_3 polar ?

Solution : Chloroform is a tetrahedral molecule, but all the bonds are not alike. Chlorine is more electronegative than hydrogen, so the C-Cl bonds are more polar than C-H bond. In this case, the complete cancellation of bond dipoles does not take place because one individual bond dipole is different from the other three. So the molecule is polar.

6.7.2. Percentage Ionic Character of Covalent Bond

The polarity of a bond can be measured by determining the dipole moments, μ (mu) of a molecule. The dipole moment of a molecule can be measured experimentally.

The measured value of the dipole moment μ of HF is 1.91 D. In SI units it will be equal to

$$= 1.91 \text{ D} \left(\frac{3.34 \times 10^{-30} \text{ Cm}}{\text{D}} \right) = 6.38 \times 10^{-30} \text{ Cm}$$

Since the bond length for HF is 92 pm ($1 \text{ pm} = 10^{-12} \text{ m}$) we can calculate the magnitude of the charges on each atom.

$$= \frac{\mu}{r} = \frac{6.38 \times 10^{-30} \text{ Cm}}{92 \times 10^{-12} \text{ m}} = 6.9 \times 10^{-20} \text{ C}$$

$$\text{Percentage ionic character} = \frac{\text{Actual charge} \times 100}{\text{Electron charge}}$$

The charge on the electron, and therefore, the total ionic charge, is $1.6 \times 10^{-19} \text{ C}$. The fraction of this unit charge that is designated ' δ ' in HF is :

$$\delta = \frac{6.9 \times 10^{-20} \text{ C}}{1.6 \times 10^{-19} \text{ C}} = 0.43$$

$$\text{Percentage ionic character} = 0.43 \times 100 = 43\% \text{ ionic}$$

Therefore, the molecule of HF is 43% ionic. The polar nature of the molecule can be understood by comparing the calculated and experimentally measured bond length.

Calculated value for the bond length is

101 pm

Measured bond length is

92 pm

This shortening of bond length is attributed to the partial ionic character of the molecule. Because of ionic character, atoms get closer, and thus, bond shortening takes place.

Attempts to relate difference in electronegativity to percentage ionic character in the bonding have also been made (Fig. 6.63).

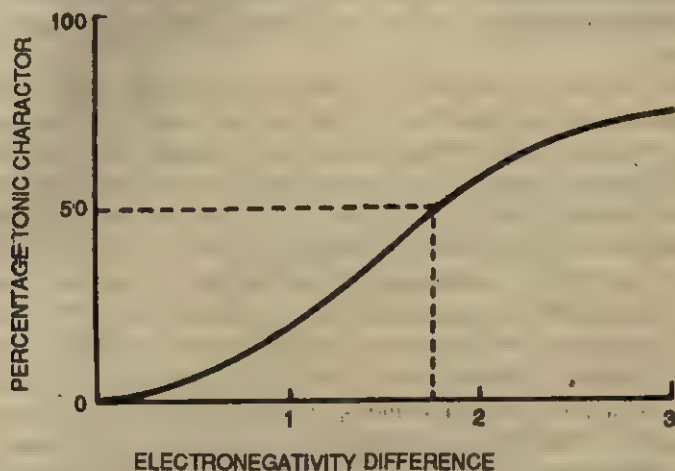


Fig. 6.63 Percentage ionic character as a function of electronegativity difference

The graph is based on the ionic characters of hydrogen halides (HF, 43% HCl 19%, HBr 11% and HI 4%) whose ionic characters are determined experimentally from dipole moments. When the electronegativity difference is about 1.7, the bond is about 50% ionic. With a difference larger than this, the bond becomes more ionic than covalent; with a difference less than this, the bond is more than 50% covalent and polar. Electronegativities can tell us whether the two atoms will tend to form an ionic bond, a polar bond or a non-polar bond. Table 6.4 is a rough guide to the relationship between the electronegativity differences of the bonding species and the percentage polarity of the bond.

TABLE 6.4 Relationship between electronegativities and polarities

Electronegativity difference	0	0.25	0.5	0.75	1.0	1.5	1.7	1.75	2.0	2.5	3.0
Percentage polarity (ionic character)	0	2	6	14	22.5	43	50	52.5	62.5	78.5	89

6.8 BONDING IN SOLID STATES

Matter is an aggregate of atoms. There are three different states or phases of matter : gas, liquid or solid.

Solids and liquids are termed condensed phases. In them the constituent atoms, molecules or ions are packed closely together with very little free space, and each is greatly affected by the behaviour of its nearest neighbours. Various types of bonding patterns have been recognized amongst the solids, viz., covalent, ionic, metallic and van der Waal's bonds.

A gas, by contrast, contains widely spaced isolated molecules. Covalent and ionic bonds are the only possibilities amongst isolated molecules.

The state of a substance, *i.e.*, whether it is a solid, a liquid or a gas, depends partly on how strongly the particles attract one another. This strength of attraction (interparticle force) depends upon whether the particles are molecules, atoms or ions. Further, it depends upon the nature and stereochemistry of the molecules. These characteristics of molecules, in turn, depend on the electronic structures of the atoms or ions involved. When intermolecular forces become sufficiently strong, molecules aggregate into clusters and a gas is converted to the liquid state and a liquid to the solid state. The difference in solid and liquid clusters is mainly ordering. The molecules in solid clusters are arranged in a definite order while molecules in liquid clusters are irregular. However, both types of clusters are formed because a drop in energy is experienced in such clusters formation. Fall in energy has already been understood as an essential condition for the formation of ionic, and covalent bonds. Through these pages we will study the various kinds of bonding involved in the formation of clusters of molecules, thus, the process of lowering of energy.

Solids tend to crystallize in definite geometric forms. The regular geometric pattern of the units (pattern of points) constituting a crystalline solid is called crystal lattice (space lattice) or simply a crystal. A lattice is a regular three dimensional arrangement of particles occupying relatively fixed positions in space. The positions which the particles occupy in the crystal lattice are called crystal lattice sites. The particles occupying the lattice sites are held in a definite arrangement by the strong interparticle attractive forces. These particles vibrate about their mean positions, and thus, distribute kinetic energy throughout the solid.

The nature of the particles occupying the crystal lattice sites depends on the nature of the solid. These particles can be atoms, ions or molecules, and hence, they may be described in terms of lattice points. For the lattice points to be equivalent, they must have the same

chemical environment. In Fig. 6.11 the three dimensional crystal lattice of sodium chloride is shown. Each Na^+ ion is surrounded by 6 chloride ions and vice versa. Thus, both Na^+ and Cl^- ions have identical environments but are different for the two ions. Therefore, in NaCl the lattice points may be labelled at the sites of either Na^+ or Cl^- ions but not at both.

Further, the particles arrange themselves as warranted by the attractive forces. These attractive forces may be electrostatic (interionic), covalent (interatomic) or intermolecular forces.

Crystals are classified on the basis of structural units - ions, atoms or molecules - and the nature of forces holding particles together in a crystal as follows :

6.8.1 Ionic Solids

One can visualize a process whereby the gaseous ion pairs of $\text{Na}^+ \text{Cl}^-$ will condense upon cooling into an orderly three dimensional array in a solid. This process leads to the release of energy called **lattice energy**. Finally formation of ionic crystalline solid takes place. Such a crystal could be possible because oppositely charged ions are held by strong electrostatic forces. Substances like, lithium fluoride, sodium chloride, and potassium chloride exist in solid state as ionic crystals (because ion units constitute the crystals). The ions may be monoatomic (Na^+ , Ba^{2+} , Cl^- , F^- etc.) or polyatomic (NH_4^+ , SO_4^{2-} , NO_2^- , etc).

The mode of packing of ions depends on the relative sizes of positive and negative ions. Generally there exists two interpenetrating lattices of anions and cations. Cations and anions of nearly the same size pack themselves in a body centred cubic fashion, e.g., CsCl . If the radius ratio of positive and negative ions is a little smaller than that of CsCl , the packing is of face centred cubic type seen in NaCl . In NaCl crystal (Fig. 6.11) the average distance between two neighbouring ions is 281 pm which is slightly less than the sum of radii of each Na^+ (95 pm) and Cl^- (181 pm). Thus, there is almost negligible space between the ions.

Strong electrostatic forces impart hard and brittle character to them. They are high melting solids with very low vapour pressures because lot of energy is required to overcome the electrostatic forces holding the charged ions. Under the influence of shearing force, planes move and orient in such a fashion so that like charges come in contact and repel one another. Thus, a crystal may suffer cracking. Ionic solids are easily broken. They do not conduct electricity as the ions are fixed in positions. In molten states they conduct electricity as the ions are free in this state. Ionic solids dissolve easily in polar solvents like water.

6.8.2 Molecular Solids

In these covalent solids, small and discrete molecules are held together by relatively weak dipole-dipole or van der Waals forces. Such solids are of two types, *i.e.*, polar and non-polar molecules.

X-ray analysis of the non-metallic solids has revealed a variety of structures. In these solids, the atoms are linked by covalent bonds.

Both HI (molecule of slight polarity) and H_2O (molecule of high polarity) are polar molecules. Polar molecules constituting crystal lattice are held by dipole-dipole attractions (Fig. 6.64).

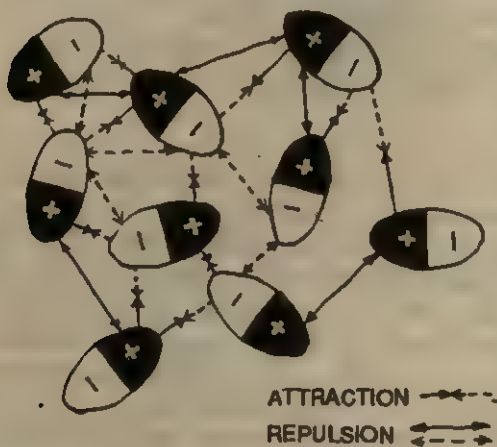


Fig 6.64 Electrostatic interactions between dipoles

permit the molecules to be separated easily. Thus, nonpolar molecular substances are low melting solids with fairly volatile nature. They are soft and can be easily broken and deformed. Molecular compounds contain neither delocalized electrons nor ions. Thus, these cannot conduct electricity when molten or dissolved in water. Solid argon, iodine, hydrogen, carbon dioxide (dry ice), naphthalene and sucrose belong to this class of solids.

The network of molecules in the molecular solids depends on the nature of molecules. We know that hydrogen molecule and similar such molecules cannot form additional covalent bonds because of the lack of vacant orbitals for further bonding. However, hydrogen liquefies and even solidifies at low temperature. It will be appropriate to know the nature of the forces operating in such molecular structures, *i.e.*, between two non-polar molecules.

The attractive forces between atoms or molecules are electrical in nature, *i.e.*, the component atoms or molecules are neutral in the

The arrangement of the polar molecules depends upon the shapes of the molecules and the strength of attraction (Fig. 6.65).

Although the atoms in non-polar molecules are joined by strong covalent forces, the separate non-polar molecules are held together by van der Waals attractive forces within the crystal lattice. These forces are relatively weak. They

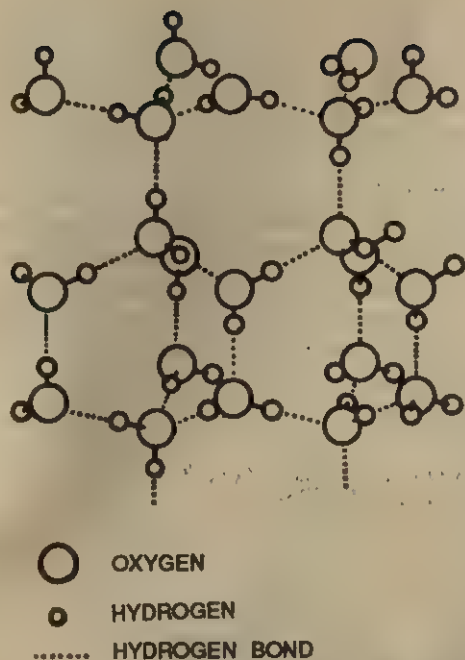


Fig. 6.65 Structure of ice, the orientation of water molecules in the ice crystal

distributed symmetrically because of their constant and continuous motion. As a result, atom or molecule will develop the characteristic instantaneous dipole, i.e., a dipole that exists temporarily. At some other moment, the electrons might have changed their positions and the polarity is different, over time, the net dipole moment becomes zero, but the atom has a fluctuating, transitory dipole moment. This has been illustrated in Fig. 6.66 through a set of figures.

When an atom (or molecule) with instantaneous dipole comes in the contact of another atom, the mutual repulsion of the two electron charge clouds results in momentary distortion or polarization of the electron charge cloud of the non-polar atom (i.e. the 2nd atom). Electrons in one atom or molecule tend to orient themselves with respect to electrons in another atom so that they stay as far apart as possible and thereby experience no mutual repulsion. An atom with fluctuating and instantaneous dipole will interact with a neighbouring atom and induces a temporary dipole in such a way that there is a net attraction between the two dipoles. Hence, two atoms become momentarily polarized, producing an electrostatic force of attraction between them, called an instantaneous induced dipole attraction. Fig. 6.67 or London

sense that their electrical charges are balanced, but the distribution of electrons in them may be such at a point of time that the electrical charges are unbalanced. Then atoms are attracted to each other.

Further, in non-polar substances such as iodine and noble gases, etc. there is no initial dipole and the molecules are electrically symmetrical. Let us consider a noble gas atom such as He or Ar with a spherically symmetrical electronic charge cloud. However, at a particular moment, electrons may not be



Spherically symmetric electron charge cloud of a He atom. The atom is non-polar because the centre of positive and negative charges coincide



Instantaneous position of the two electrons in a He atom causing a temporarily polar atom. Centres of positive and negative charge do not coincide



A different type of instantaneous position of the two electrons in a He atom, causing a separate temporary polarity

Fig. 6.66 The fluctuating dipole in a helium atom. The helium atom is non-polar; its dipole moment is zero

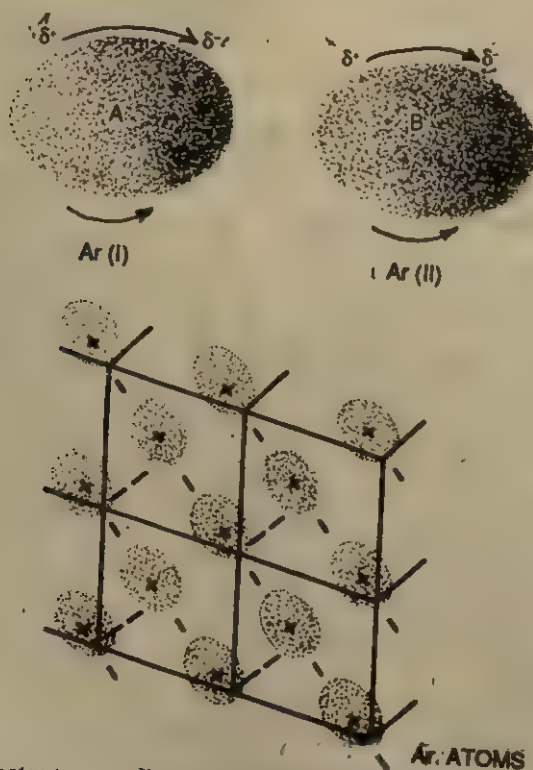


Fig. 6.67 Instantaneous dipole- instantaneous induced dipole interactions or London dispersion forces : As the instantaneous dipole in atom A appears, it induces a dipole in atom B

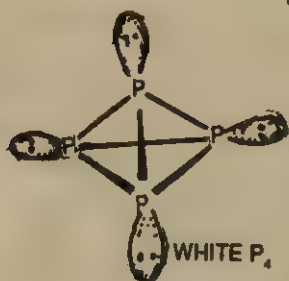
dispersion force. Collectively all these weak forces are called van der Waal s forces.

Phosphorus exists in a number of allotropic forms. The most common variety is yellow (or white) phosphorus. Phosphorus (solid at room temperature) exists as discrete molecule, P_4 . Its tetratomic (P_4) molecule is with each P atom at the corner of a regular tetrahedron (Unit 12). The tetrahedra are held together by van der Waal s forces.

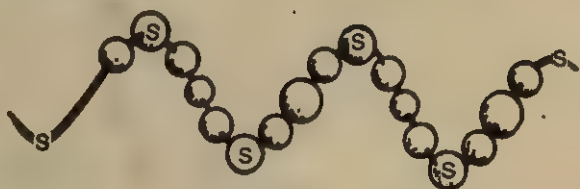
Rhombic sulphur (most common variety and solid at room temperature) consists of puckered eight membered rings (S_8) ; each atom being covalently bound to two others. The discrete S_8 molecule is weakly bonded in lattices by van der Waal s forces (Unit 13). In another variety of sulphur, i.e., plastic sulphur, atoms are arranged in spiral chains, the chains being held parallel to each other by van der Waal's forces. This is an amorphous solid derived from a supercooled liquid.



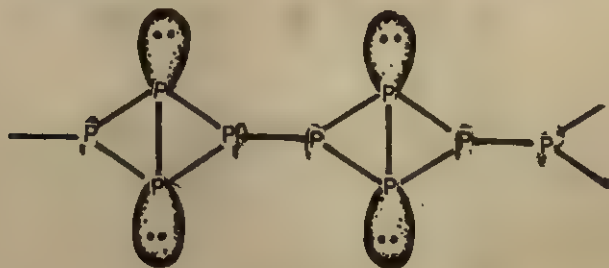
S_8 MOLECULES



WHITE P_4



PLASTIC SULPHUR



RED PHOSPHORUS

In molecular chlorine, orthorhombic diatomic molecules are joined by weak intermolecular forces. The solid is easily vapourized, indicating weak intermolecular forces.

In solid inert gases, atoms are held by weak interatomic forces. Argon is known as individual atom.

Van der Waals forces are responsible for the condensation of inert gases, and other gases such as hydrogen, oxygen, nitrogen and methane, etc. which are devoid of any residual bonding power. In all such cases, liquid and solid clusters are formed through these weak forces. Solids so produced have molecules as individual units. Such solids are, therefore, called molecular solids.

6.8.3 Covalent (Atomic) Solids

In these solids, neighbouring atoms are held by covalent bonds. The network of atoms bonded by covalent bonds grow in size in fixed directions to form a giant molecule. It is difficult to distinguish individual molecules in such structures. The units in these giant molecules can either be atoms of the same element or atoms of different elements with matching electronegativities. Diamond, germanium, carborundum (SiC), quartz (SiO_2), etc. belong to this class of solids. Since the atoms are held by strong covalent bonds the crystals are very hard, non-volatile, poor electrical conductors and have very high melting and boiling points and resist deformation. In the three dimensional structure of diamond, each carbon atom is covalently bonded to four other carbon atoms arranged tetrahedrally (Fig. 6.68). Every carbon

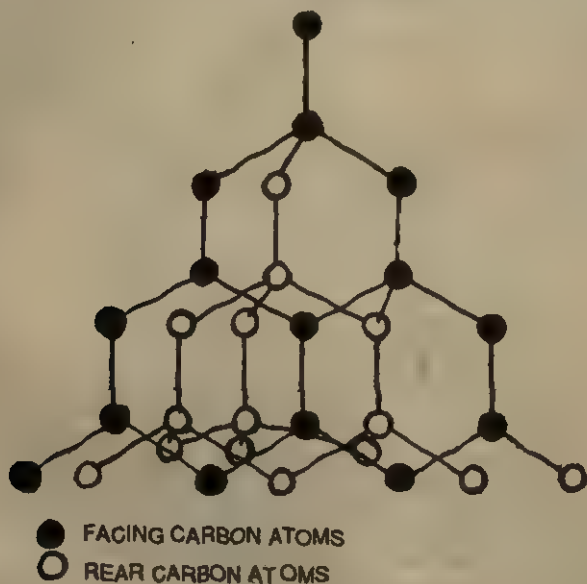


Fig. 6.68 The crystal structure of diamond - All C-C bond lengths are 154 pm

atom forms four covalent bonds by sharing electrons with each of its four nearest neighbours. Each bond is formed by the overlap of two sp^3 hybrid orbitals located on adjacent atoms. The giant molecular structure which results is very strong. Silicon carbide (SiC) and boron nitride (BN)_n also form crystals with a diamond like structure.

Silicon has a diamond-like structure. It is fragmentary and not continuous due to weak bonds. In this, each Si atom is surrounded tetrahedrally by four others. This has extremely high melting and boiling points.

Silicon dioxide (silica) also forms a three dimensional structure. The Si-O bonds about each silicon atoms are tetrahedrally distributed and each oxygen atom is bonded to the other silicon atoms. This structure is also associated with quartz and other crystalline form of silica (Unit 12).

Graphite, the other allotrope of carbon, also belongs to this class of solids. It has a layered structure. Each carbon atom is covalently bonded to three other carbon atoms in its layer through three coplanar sp^2 hybrid orbitals resulting in a sheet like structure. In a layer, the carbon atoms are bonded in a hexagonal network. Layers are held by weak van der Waals forces. These forces allow one layer of bonded atoms to slide over another layer. The layer structure (Fig. 6.69) accounts for the properties of graphite. It is lubricant, whereas diamond is abrasive. The strong bonds within the layers are responsible for its high melting point. The unhybridized p electrons form a delocalized cloud of electrons similar to the metallic bond. This enables graphite to conduct electricity and show its shiny appearance.

6.8.4 Metallic Solids (Metals)

Over eighty percent elements in the periodic table are metals. Metals are solids at ordinary pressures and temperatures except mercury (m.p. 234K) and gallium (m.p. 302.8K)

Metallic elements acquire one of the three packings listed below in their crystalline forms :

- (i) Body centred cubic packing (bcc) - Na
- (ii) Hexagonal closet packing (hcp) - Mg
- (iii) Face centred cubic closest packing (fcc) - Al

Metallic atoms are distributed in a regular and definite pattern which depends on the size and electronic configuratin of the atoms constituting the solids. The structural units are positive metal ions which are held strongly by the strong electrostatic forces between positive metal ions and mobile valence electrons. Thus, their melting and boiling points are moderately high. Metals range from rather soft, low density, low melting solids such as Li and Na to hard, dense, high melting solids such as tungsten.

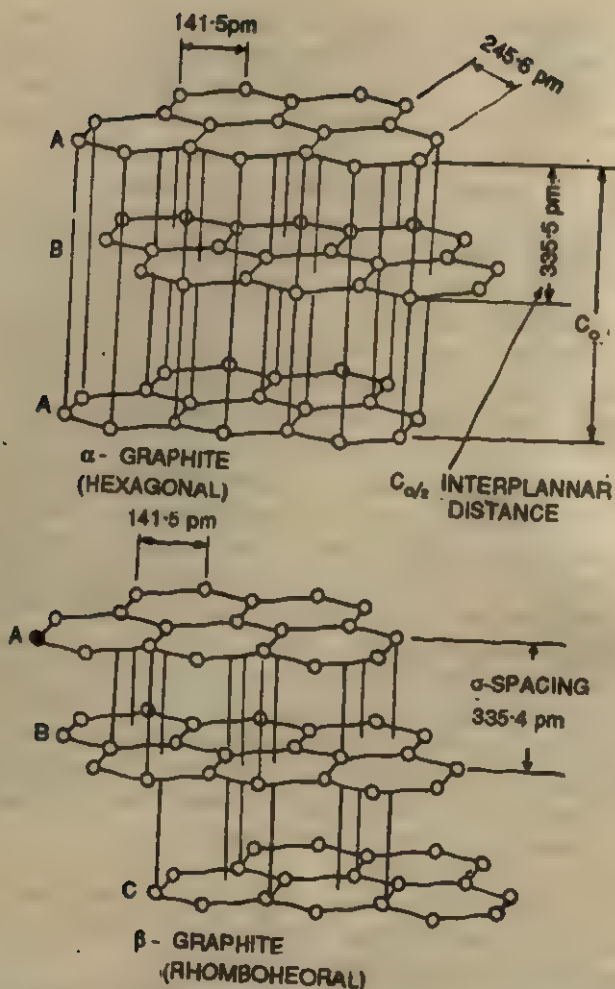


Fig. 6.69 The graphite structure (hexagonal) and (rhombohedral) forms of graphite

Metals play a vital role in the economy of a country and in modern civilization. They are the backbone of industry and technology. It will be of immense help to investigate the nature of bonding in metals and thus, to correlate the characteristic properties of metals with bonding.

Metallic Bond

Theories of ionic and covalent bonding do not account for the strong bonding in metals. Structural studies have shown that in all metallic crystals the atoms are close packed or nearly so, having either eight or twelve nearest neighbours. Each metallic atom has one, two

or at the most three electrons in its valence shell which can be used for binding purposes. Hence, normal covalent bonds cannot hold these atoms together as insufficient number of electrons are available. Solid lithium has *bcc* packing, i.e., Li atom is surrounded by eight atoms of lithium. The presence of one electron in its valence shell ($1s^2, 2s^1$) is not capable of binding eight more atoms through electron pair covalent bonds. Similar type of atoms cannot provide ionic bonding because of the lack of difference in electronegativity. Metals are too strong to be held together by weak van der Waals forces. The concept of metallic bond is, therefore, introduced to describe satisfactorily the bonding in metals.

Most metals, because of their low ionization energies, lose one or more of their valence electrons and change into positive ions. These emitted electrons do not remain localized. They are mobile and bind the positively charged ions (called metallic kernels) together by electrostatic forces. The metal, thus, may be considered as the crystal lattice (three dimensional array) of closely packed positive metal ions dispersed in a 'sea' of very mobile electrons. The electrons move in such a fashion that they are at a time near to two or more kernels and provide the binding forces required to keep the metal ions in position. The lowering of energy is attributed to the attractive interaction between the negatively charged electron and the positively charged lattice.

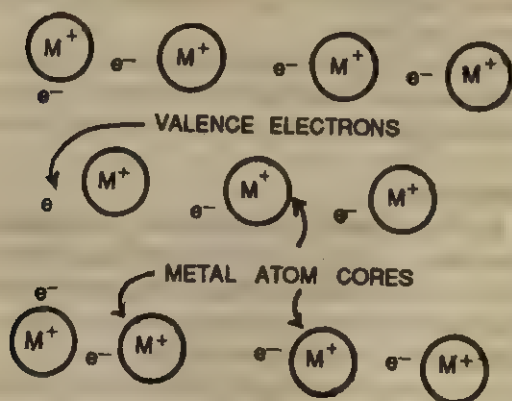


Fig. 6.70 A simple picture of metallic bonding (Electron 'sea' model)

electrons move more or less freely in an applied electric field towards the positively charged side of the conductor causing the electrical con-

This type of bonding is called metallic bonding. It is partially electrostatic in nature. The total number of electrons will be equal to the sum of the positive charges in the metal ions.

Properties of metals have been included in Unit 12. Many of these metallic properties depend on high mobility of the delocalized electrons. The

duction. The conduction of heat is also related to electron flow as electrons acquire kinetic energy when one portion of the metal is heated.

Unlike covalent bond, a metallic bond has no directional character. The movement of positive ions with respect to one another without seriously disturbing the bonding within the metal makes feasible the deformation of the metals without fracture. This explains the malleability and the ductility. Under stress, the metal changes shape as layers of atoms slide over each other. On removing the stress, the atoms assume their original state. This explains the elasticity.

Light striking a metallic surface is absorbed by loosely bonded electrons at the surface. These electrons oscillate back and forth and emit radiant energy in the form of visible light. This absorption and emission by the mobile oscillating electrons imparts a characteristic luster to metals. Hence, a smooth or polished metal has a good reflecting surface.

The strong electrostatic attractions between the positive ions and the sea of electrons that bonds the atoms strongly into the lattice are responsible for the high tensile strength of metals (i.e., they resist stretching without breaking).

Some metals are soft (*bcc*) and some are hard (efficient packing *hcp* and *ccp*) and brittle. The softness of alkali metals is explained by the relatively small number of electrons per atom available for metallic bonding in the crystal, so the coulombic attraction forces are minimum. The relatively low boiling and melting points of these soft metals are consistent with this explanation.

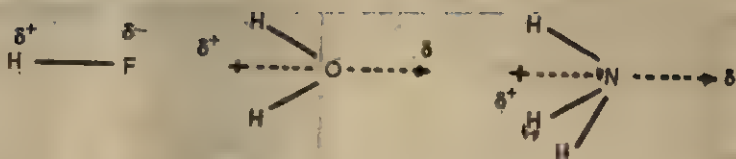
In the case of hard metals, large number of electrons per atom are involved in the metallic bonding. The coulombic attraction forces are much stronger which exert greater restraint on the distortion of the crystal structure.

6.9 HYDROGEN BONDING

There is a great deal of evidence to indicate that a hydrogen atom interacts with two other small, highly electronegative atoms which have lone pairs of electrons, such as nitrogen, oxygen and fluorine to an extent greater than corresponds to normal van der Waals bonding. Such an interaction is called hydrogen bonding.

This type of bond can be explained in electrostatic terms. When hydrogen is covalently bonded to one of the electronegative atoms, F, O or N, the bond is polar and a dipole moment is set up.

The covalently bonded hydrogen atom carrying a fractional positive charge in these molecules is capable of attracting the negative end of another dipole on the neighbouring molecule, and so on, so that the molecules become associated. It has been suggested that this oc-



curs by an interaction between the positive end of the dipole and a lone pair of electrons on the electronegative atom. This situation in HF is shown in Fig. 6.71. The molecule may be described as (HF) $_n$.

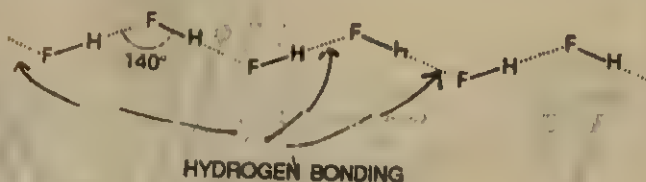


Fig. 6.71 The structure of solid hydrogen fluoride - resulting from hydrogen bonding.

The hydrogen bonding holds a number of molecules of HF together in liquid hydrogen fluoride. The hydrogen bond is usually represented by a dotted line.

Hydrogen bonding is different from dipole-dipole interactions seen in other polar molecules. A hydrogen atom has no inner, non-bonding electrons to set up forces of repulsion with the non-bonding electrons of the other atom. The strength of the hydrogen bond is in the range 25 - 35 kJ mol⁻¹. It is much stronger than the van der Waal s/force (about ten times) but weaker (about 1/10 to 1/20) than the average covalent bond. It has a great significance in accounting for the properties of various substances.

The simple evidence for the existence of hydrogen bonding comes from comparisons of melting and boiling points in series of hydrides (Fig. 6.72).

It can be seen from the Fig 6.72 that the melting and boiling points of the hydrides of group 14 increase as the relative molecular mass increases (van der Waal's attraction increases with an increasing number of electrons). However, the lowest molecular mass hydride in each of the groups 15, 16 and 17 has abnormally high melting and boiling points. This shows that some extra intermolecular attraction

MELTING POINT

BOILING POINTING

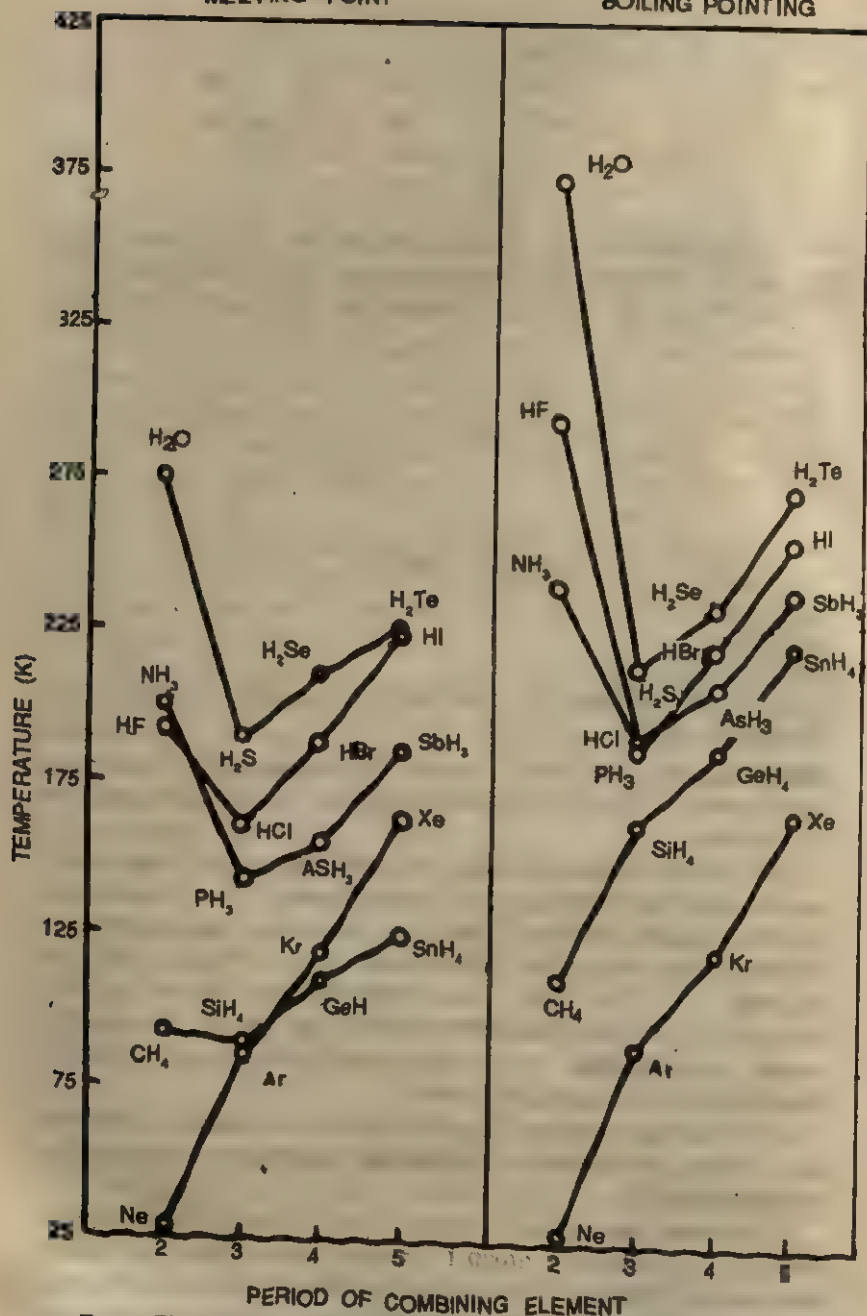


Fig. 6.72 Melting and boiling points of the molecular hydrides and the noble gases.

must be involved in these substances. A similar pattern can be seen in the enthalpies of vapourisation of the liquid hydrides (Fig. 6.73). The

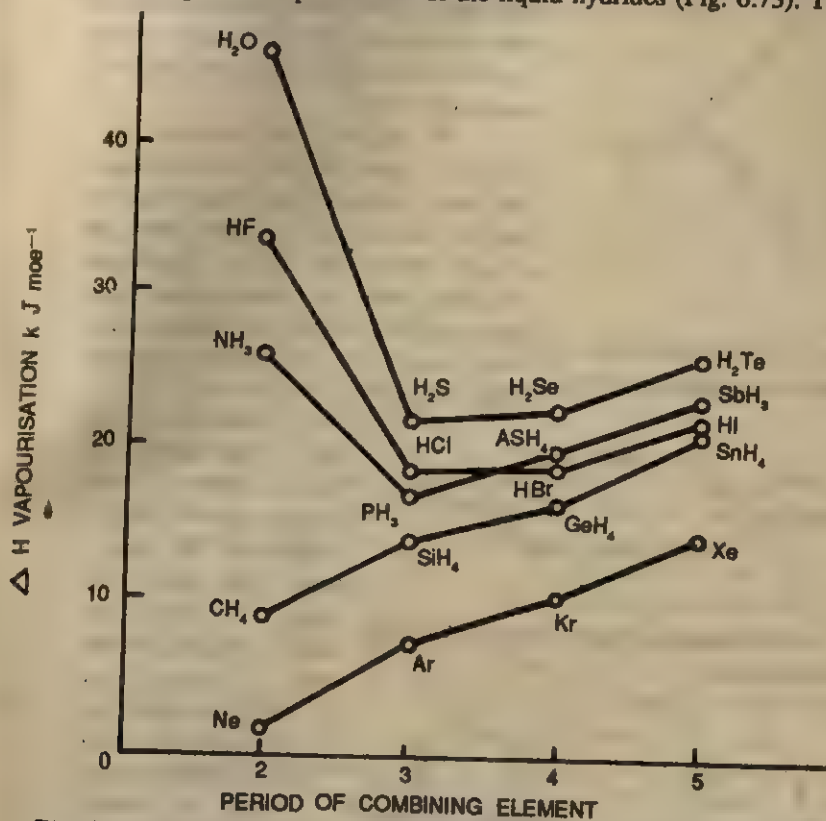


Fig. 6.73 Enthalpies of vapourisations of molecular hydrides and noble gases at their boiling points

abnormally high melting and boiling points and high enthalpies of vapourisation of the first member in each of the groups 15, 16 and 17 (i.e., NH_3 , H_2O , and HF) arise because the energy is required to break the intermolecular forces. Since fluorine, oxygen and nitrogen are the most electronegative of the elements in their corresponding groups, the inter-molecular forces are thought to be hydrogen bonds. Nitrogen and oxygen atoms in these molecules do not pull electrons as strongly as fluorine, but they are electronegative enough to enable the formation of hydrogen bonds.

Water is the most familiar substance which exhibits hydrogen bonding. It is extensively hydrogen bonded. No free H_2O molecules is likely to be in the liquid state. Each water molecule is hydrogen bonded to four other water molecules (Fig. 6.74). Ice is hydrogen bonded crystal.



Fig. 6.74 Hydrogen bonding between water molecules

Hydrogen bonding between water molecules explains the structure and low density of ice and the expansion of water below 4°C (277 K) apart from the exceptionally high boiling and melting points of water.

The structure of chemical compounds is also affected by hydrogen bonding. Acetic acid and many dibasic organic acids exist in liquid phase as dimers (Fig.6.75) due to hydrogen bonding. Some compounds can form intramolecular hydrogen bonds between two groups in the same molecule (Fig.6.76).

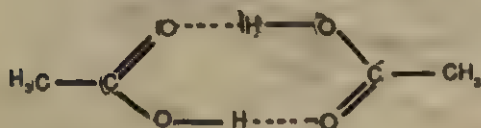
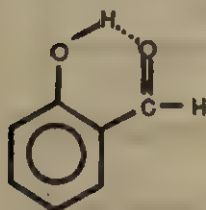
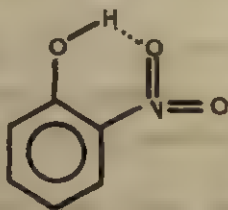


Fig. 6.75 Intermolecular hydrogen bonding in acetic acid.

Hydrogen bonding is responsible for the solubilities of some compounds of nitrogen, oxygen and fluorine in water (or protic solvents). Alcohol dissolves in water as molecules of ethanol can displace water molecules in association. New hydrogen bonds are formed between molecules of water and ethanol.



(a)

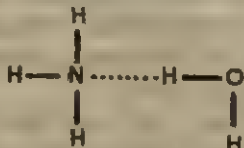
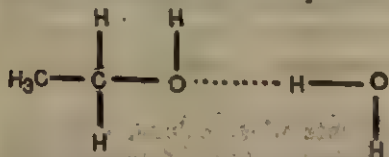


(b)

Fig. 6.76 Intramolecular hydrogen bonding in (a) salicylaldehyde and (b) nitrophenol

Hydrogen bonding has a vital role to play in the structure of some

biological materials such as proteins and nucleic acids (Unit 19).

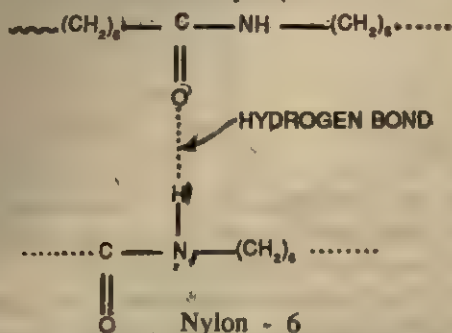


Without hydrogen bonds the proteins would lose most of their important structural and physiological properties.

Since proteins occur in a wide variety of biological materials,

(e.g., muscle, hair, enzymes, etc.) we are, thus, dependent on the hydrogen bonds in living systems.

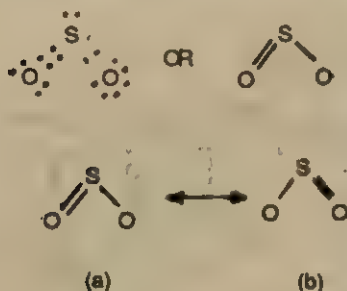
Hydrogen bonding contributes towards the strength of nylon. The chains are held together through hydrogen bonds.



Nylon and polythene have very different textile strengths. Polythene has no hydrogen bonding.

6.10 RESONANCE

It often happens that a single satisfactory Lewis structure for a molecule or ion cannot be portrayed. For example, two Lewis structures that obey the octet rule can be drawn for sulphur dioxide.



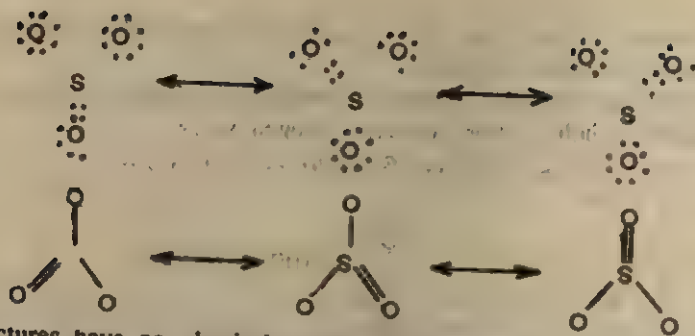
In these two structures each atom fulfils the octet rule. They differ in the arrangement of electrons. In both, one oxygen atom is attached through a single bond to sulphur atom while

the other oxygen atom is joined through a double bond. It means that the two bonds are different. But all experimental evidence show that both the linkages be-

tween S and O are identical and have properties that lie somewhere between those expected for single and double bonds. Thus, we are forced to conclude that neither of the Lewis structures for SO_2 is satisfactory.

To explain such type of structures, the concept of resonance is introduced. The actual molecule is visualized as some intermediate or resonance hybrid of the two structures, (a) and (b) (called resonance structures or canonical forms). The sign \longleftrightarrow represents the resonance between the two resonance structures. Some species cannot be adequately described with two resonance structures. SO_3 molecule requires three structures.

The concept of resonance is very helpful in describing the structures of unsaturated compounds in organic chemistry. Resonance

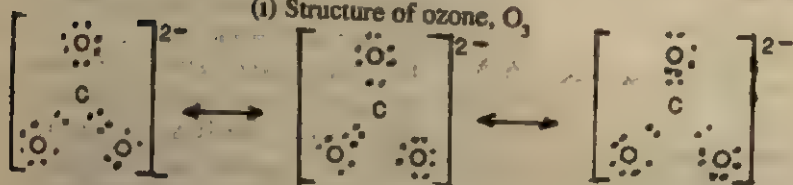


structures have no physical reality. It is difficult to prepare them. These are only imaginary structures. Some more examples of resonance structures are illustrated below (Fig. 6.77).

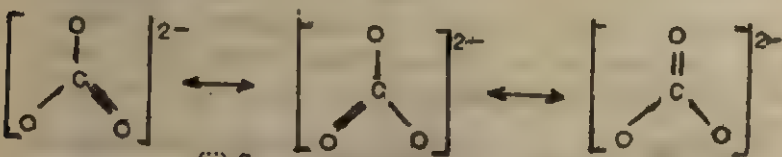
Thus, resonance is a way of describing the structures of molecules that cannot be adequately represented by a single Lewis structure because the electrons are not localized as shown in a Lewis structure. Such a molecule may be portrayed by a combination of two or more Lewis structures called resonance structures.



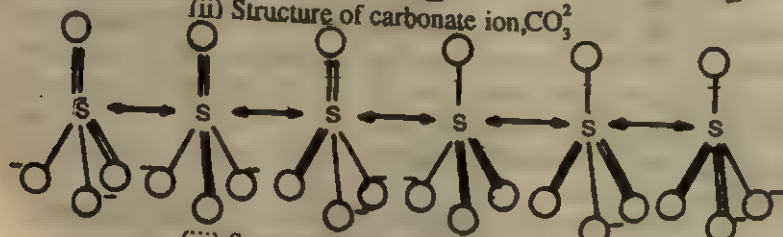
(i) Structure of ozone, O_3

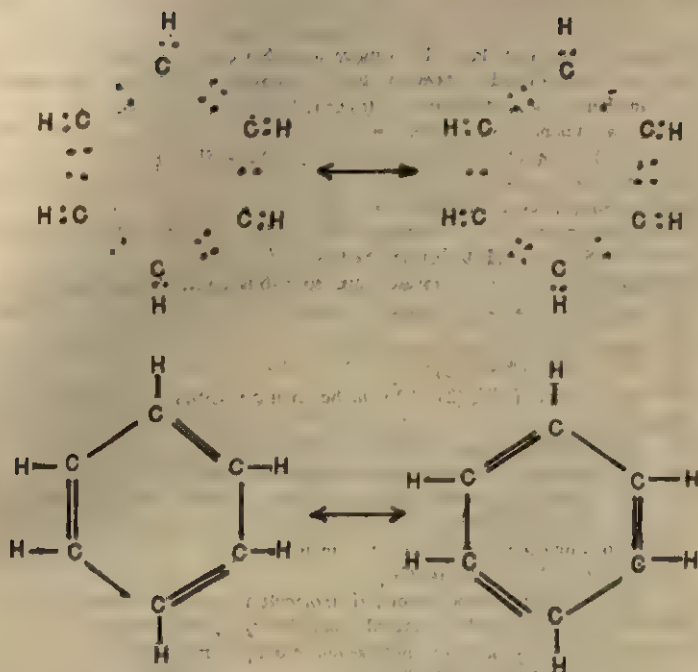


(ii) Structure of carbonate ion, CO_3^{2-}



(iii) Structure of sulphate ion, SO_4^{2-}





(iv) STRUCTURE OF BENZENE C_6H_6

Fig.6.77 Resonance structures of (i) O_3 , (ii) CO_3^{2-} (iii) SO_4^{2-} , and (iv) C_6H_6

SELF ASSESSMENT QUESTIONS

MULTIPLE CHOICE QUESTIONS

6.1 Put a tick (✓) mark against the suitable choice.

- (i) Two atoms A and B with electronic configuration 2, 8, 8, 2 and 2, 8, 7 respectively form a molecule. What will be the formula of the molecule?
(a) AB (b) AB_2 (c) A_2B (d) BA.
- (ii) Which of the followings illustrate the bonding in O_2 ?
(a) Two electrons are shared, (b) Four electrons are shared (c) Electron is transferred, (d) Electrons are not shared.
- (iii) A cation is formed,
(a) by sharing a pair of electron, (b) by donating an electron (c) by accepting an electron (d) by accepting a proton.
- (iv) Electrovalent compounds conduct electricity when dissolved in water because,
(a) their ions are free in solution (b) their ions form aggregates in solution, (c) the crystal structure persists (d) electrons are supplied by water.
- (v) Resonance structures of a molecule should have, (IIT 1984)
(a) identical arrangement of atoms (b) nearly the same energy content, (c) the same number of paired electrons (d) identical bonding

- (vi) On hybridization of one s and p orbitals we get, (IIT 1984)
 (a) two mutually perpendicular orbitals (b) two orbitals at 180° (c) four orbitals directed tetrahedrally (d) three orbitals in a plane.
- (vii) The bond between two identical non-metal atoms has a pair of electrons
 (a) unequally shared between the two (b) transferred fully from one atom to another (c) with identical spins (d) equally shared between them.
- (viii) The hydrogen bond is the strongest in (IIT 1986)
 (a) $\text{O} - \text{H} \cdots \text{S}$ (b) $\text{S} - \text{H} \cdots \text{O}$ (c) $\text{F} - \text{H} \cdots \text{F}$ (d) $\text{F} - \text{H} \cdots \text{O}$
- (ix) The hybridization of sulphur dioxide is (IIT 1986)
 (a) sp, (b) sp^2 , (c) sp^3 (d) dsp^2
- (x) The electronegativity of the following elements increases in the order (IIT 1987)
 (a) C, N, Si, P (b) Si, P, C, N (c) N, Si, C, P (d) P, Si, N, C
- (xi) The species in which the central atom uses sp^2 hybrid orbitals in the bonding is
 (a) PH_3 (b) NH_3 (c) CH_4 (d) SbH_3 (IIT 1988)
- (xii) The molecule that has linear structure is (IIT 1988)
 (a) CO_2 (b) NO_2 (c) SO_2 (d) SiO_2
- (xiii) The boiling point of NH_3 (240 K) is higher than the boiling point of PH_3 (85.3 K) because
 (a) the molecular weight of NH_3 is less than that of PH_3
 (b) London dispersion forces are stronger for NH_3 than for PH_3
 (c) the vapour pressure of NH_3 is greater than the vapour pressure of PH_3
 (d) NH_3 is hydrogen bonded, but PH_3 is not (e) NH_3 is polar, but PH_3 is not.
- (xiv) π bonding occurs in each of the followings except
 (a) CO_2 (b) C_2H_4 (c) C_6H_6 (d) CH_4
- (xv) The geometrical structure of NH_3 molecule is (a) square planar (b) trigonal bipyramid (c) tetrahedral (d) trigonal pyramidal (e) trigonal planar
- (xvi) Which of the following compounds has the zero dipole moments?
 (a) CH_4 (b) NH_3 (c) NF_3 (d) CH_3Cl
- (xvii) In which of the following compounds do the bonds have the largest percentage of ionic character?
 (a) N_2O_4 (b) H_2O (c) HF (d) CO_2
- (xviii) In which of the following compounds does every atom has eight electrons in its valence shells?
 (a) CH_4 (b) SF_4 (c) PCl_5 (d) BF_3
- (xix) Which of the following hydrides has the largest bond angle $\text{H}-\text{M}-\text{H}$?
 (a) H_2O (b) H_2S (c) H_2Se (d) H_2Te
- 6.2 Indicate if the following statements are true or false by writing T or F.
- The $\text{H}-\text{N}-\text{H}$ bond angle in NH_3 is greater than the $\text{N}-\text{As}-\text{H}$ bond angle in AsH_3 .
 - All molecules with polar bonds have dipole moment. (IIT 1984)
 - Graphite is a better lubricant on the moon than on the earth.
 - sp^2 hybrid orbitals have equal s and p character. (IIT 1987)
 - The reactivity of an atom is determined by its electronic configuration.
 - Ionic compounds are formed by the transfer of electrons, whereas covalent compounds are formed by the sharing of electrons.
 - The shared pair of electrons is always shared equally in a covalent compound.
 - Octet rule is always helpful in explaining the structures of various molecules.
 - Hydrogen chloride is a polar molecule.
 - The bond angles in CH_4 and SiH_4 are equal.
 - The strength of the σ bond and π bond is always equal.
 - Oxygen is both diamagnetic and paramagnetic in nature.
 - There is a large build up of electron density between the atoms which bonds them together.
 - For water, ammonia and methane, the bond angle is 109° .

15. Both NCl_3 and BCl_3 have same number of covalent bonds but they adopt different geometry.
- 6.3 Fill in the blanks with the most appropriate words.
- compounds are formed by complete transfer of
 - In a HCl molecule, the shared pair of electrons is shared, hence..... develops in the molecule.
 - Mutual sharing of electrons between two atoms gives rise to bond.
 - A bond in which one atom donates both electrons of the shared pair is called a covalent bond.
 - HF is more polar than HCl , so it should have melting and boiling points than HCl
 - In carbon one s and three p orbitals mix to form four and bonding orbitals.
 - The polarity of a covalent bond can be measured by determining the
 - The true structure of a molecule exhibiting is a to which Lewis structures constitute.
 - The electrostatic attractions and repulsions in ionic crystals result in of the solid.
 - The dipole-dipole attractions including are the
- 6.4 Match the following choosing one item from column X and the appropriate item from Column Y.

Column X	Column Y
1. Malleability	(i) Percentage ionic character
2. Dipole moment	(ii) Non-polar
3. Water	(iii) sp^2 hybridization
4. Symmetric molecules	(iv) Side to side overlapping of orbitals
5. Graphite	(v) Hydrogen bond
6. Sigma bonds	(vi) p orbitals
7. Pi bonds	(vii) End to end overlapping of orbitals
8. Molten state	(viii) Emission of radiations
9. Directional in nature	(ix) Conducts electricity
10. Metals	(x) Metals
11. A high melting network solid	(xi) Solid argon
12. Nonconducting solid which in its molten state behaves as a good conductor	(xii) CsCl crystal
13. A solid which has high electrical and thermal conductivity	(xiii) Germanium metal
14. A low melting solid held together by van der Waals forces	(xiv) Lithium metal
15. A solid in which hydrogen bonding exists	(xv) Ice

SHORT ANSWER QUESTIONS

- 6.5 (a) What type of bonding would you expect in the following sets when two atoms, A and B with the given electronic structures combine with each other?
- A = 2, 8, 1 B = 2, 7
 - A = 2, 8, 8, 2 B = 2, 6
 - A = 2, 8, 7 B = 2, 8, 7
- (b) In forming a compound XY , atoms of X lose one electron each while the atoms of Y acquire one electron each. Predict the nature of the compound and give its two properties.
- (c) Assume that one electron has been removed from each of the atoms, Li, Na, K to form Li^+ , Na^+ and K^+ and that one electron has been added to F and Cl atoms to form F^- and Cl^- . Give the electronic configuration for all these ions. Mention the noble gases which can represent these electronic configurations.
- (d) Which electrons take part in bond formation?

(e) Which of the following pairs do you expect to be a polar molecule ?

(i) CCl_4 or HCl (ii) CO or CO_2

(f) Choose the ionic compounds of the following compounds ?

(i) Cl_2 (ii) MgCl_2 (iii) AlF_3 (iv) NH_3 (v) CO_2 (vi) CH_4 (vii) MgO (viii) CaCl_2

(g) (i) If X and Y have the following electronic configurations, how many atoms of the element X will combine with one atom of Y ?

X = 2, 8, 7, Y = 2, 4

(ii) Give the Lewis structure of the compound

(iii) What would be the nature of the bond formed between X and Y?

(iv) Name the compound

(h) Write briefly answers of the followings

1. Graphite is a conductor but diamond is not

2. Diamond is the hardest substance known

3. An oxygen molecule is paramagnetic

4. Water is a liquid at ordinary temperature whereas H_2S is a gas.

(i) Draw Lewis structures for the following molecules and ions.

F_2 , PH_3 , H_2S , F_2O , K^+ , Br^- , SiF_4

(j) Three elements are represented by the following Lewis symbols.

K^\bullet , $:\text{L}^\bullet$ and $:\text{M}^\bullet$

(i) Assign the appropriate group in the periodic table

(ii) Which elements are likely to form ions? Give the charges carried by ions.

(iii) Give the correct formulae and electron dot structures of the covalent compounds formed between (a) K and L, and (b) K and M.

6.6 (i) Identify the atoms in each of the listed compounds/ions which do not follow the octet rule,

SO_2 , PCl_5 , BF_4^- , PCl_3 , H_2S , SF_6 , SF_4 , BeF_2 , SCl_2 , CO_2 .

(ii) Predict the shapes of the following molecules/ions on the basis of VSEPR theory.

BeCl_2 , SiF_4 , AsF_3 , H_2Se , HgCl_2 , BF_4^- , SF_6 , ClF_3 , SO_3 , SO_3^{2-}

(iii) Sulphur dioxide has dipole moment. What will be the shape of the molecule? Give reasons for your answer.

(iv) Predict the dipole moment of

(a) Molecule of the type of AX_4 with square planar arrangement of X atoms

(b) A molecule of the type AX_5 with a trigonal bipyramidal arrangement of atoms.

(c) A molecule of the type AX_6 with an octahedral shape.

(d) AX_2E_3 molecule with three sets of lone pairs of electrons (E_3).

(e) AX_4E_2 molecule with 2 sets of lone pair of electrons (E_2).

(v) A crystalline solid dissolves in CS_2 and is insoluble in water. It does not conduct electricity. It melts at 368K. The melt also does not conduct electricity. Its viscosity is comparable to that of water. Name the compounds which possess all these properties

TERMINAL QUESTIONS

6.1 Illustrate the inadequacy of octet rule.

6.2 What shapes are associated with the following hybridizations? sp , sp^2 and sp^3 . Give two examples of each. What angles exist between the orbitals ?

6.3 How is a covalent bond formed? Give the dot formulae for, O_2 , CO_2 , C_2H_2 , BF_3 and NH_3 .

6.4 Explain the formation of covalent bond between two hydrogen atoms. Why is such a bond not formed between two He atoms?

6.5 Explain the following terms : (i) sigma bond, (ii) pi bond, (iii) hybridization, and (iv) bond energy.

- 6.6 Give suitable examples of sigma bond formation which involve, (i) s-s overlapping, (ii) s-p overlapping, and (iii) p-p overlapping.
- 6.7 What is meant by hybridization of atomic orbitals? How does it explain the shapes of molecules? Illustrate your answer with suitable examples.
- 6.8 What is VSEPR theory? How does it explain the bond angles observed with CH_4 , NH_3 and H_2O ?
- 6.9 What happens to energy if a chemical bond is to form between two atoms as they approach each other? Illustrate.
- 6.10 Discuss the valence bond theory for the formation of hydrogen molecule
- 6.11 (a) List the various characteristics of ionic and covalent compounds.
(b) Which of the many electrons are involved in the bond formation? Explain.
- 6.12 (a) Differentiate between electrovalency and covalency.
(b) Explain the formation of cations and anions in electrovalent compounds.
- 6.13 (a) Indicate the nature of bonding in the following compounds :
 MgO , CaS , NaBr , CHCl_3 , CCl_4 , HCl , ICl , H_2O and NaOH . Also list the polar compounds.
(b) Draw Lewis structures for the following compounds: MgCl_2 , NH_3 , CaO , CHCl_3 , H_2SO_4 , NaCl .
- 6.14 Describe the changes in molecular shape that take place after the completion of the following reactions :
(a) $\text{BF}_3 + \text{F}^- \longrightarrow \text{BF}_4^-$ (b) $\text{C}_2\text{H}_2 + \text{H}_2 \longrightarrow \text{C}_2\text{H}_4$
(c) $\text{PCl}_3 + \text{Cl}^- \longrightarrow \text{PCl}_4^-$ (d) $2\text{BrF}_3 + \longrightarrow \text{BrF}_4^- + \text{BrF}_2^+$
- 6.15 (a) Why are some covalent bonds polar? What is a dipole?
(b) How can a molecule that has polar bonds be a nonpolar molecule?
- 6.16 Which of the followings are polar molecules/ions? Give reasons for your answer.
 SO_2 , SO_3 , SF_6 , ICl_2^- , H_2S , NH_3
- 6.17 (a) Explain why NF_3 has a dipole moment and BF_3 does not.
(b) Explain why NH_3 is more polar than NF_3 ?
- 6.18 How does the metallic bond explain the lustrous property, thermal conductivity and electrical conductivity of metals?
- 6.19 (a) Why is it necessary to suggest use of hybrid orbitals in explaining the structure of CH_4 ?
(b) Which of the following solids are molecular solids and which are network solids?
 C , S_8 , $(\text{BN})_n$, Ar , CsCl , MgO , P_4O_6 , Ice , I_2
- 6.20 Explain the difference in electrical conductivity exhibited by metals, ionic solids, molecular solids, and covalent solids.
- 6.21 List the properties of a substance that will be influenced by the existence of bonds.
- 6.22 What is a hydrogen bond? How can we account for the unusually high boiling points for H_2O , NH_3 and HF ?
- 6.23 (a) State the reasons for postulating the existence of hydrogen bonds
(b) Explain the importance of hydrogen bond in one's every day life.
- 6.24 (a) Define briefly each of the followings
(i) Dipole - dipole attraction (ii) Instantaneous dipole- instantaneous induced dipole attraction, and (iii) Lattice
(b) Explain the differences between liquids and solids in terms of atomic aggregates and freedom of motion of their particles.
(c) What are types of crystals? Give two examples of each type.
- ANSWERS TO SELF ASSESSMENT QUESTIONS**
- 6.1 (i) b (ii) (b), (iii) (b), (iv) (a), (v) (a), (b), (c) (vi) (b) (vii) d, (viii) (d) (ix) (b), (x) (b) (xi) (c) (xii) (a) (xiii) (d), (xiv) (d) (xv) (d) (xvi) (a) (xvii) (b), (xviii) (a), (xix) (a)
- 6.2 1. T, 2. F, 3. T, 4. F, 5. T, 6. T, 7. F, 8. F, 9. T, 10. T, 11. F, 12. F, 13. T 14. F, 15. T.

- 6.3 1. ionic, electrons 2. not equally, polarity 3. covalent 4. coordinate 5. higher, 6. different, equivalent, 7. dipole moment 8. resonance, hybrid, 9. lattice energy 10. hydrogen bonds, very weak van der Waals forces or very weak London dispersion forces
- 6.4 1. (x) 2. (i) 3. (v) 4. (ii) 5. (iii) 6. (vii) 7. (iv) 8. (ix) 9. (vi) 10. (viii) 11. (xiii) 12. (xii) 13. (xiv) 14. (xi) 15. (xv)
- 6.5 (a) (i) Ionic bonding (ii) Ionic bonding (iii) Covalent bonding (b) Compound XY is ionic in nature. Its ions are held by strong electrostatic forces of attraction. It is soluble in water.

(c) $\text{Li}^+ =$	2	Represents	He
$\text{Na}^+ =$	2, 8	Represents	Ne
$\text{K}^+ =$	2, 8, 8	Represents	Ar
$\text{F}^- =$	2, 8	Represents	Ne
$\text{Cl}^- =$	2, 8, 8	Represents	Ar

(d) Valence electrons present in the outermost shell.

(e) (i) HCl (ii) CO

(f) Ionic compounds : (i) MgCl_2 , (iii) AlF_3 , (vii) MgO and (viii) CaCl_2

(g) (i) Four atoms of X will unite with one atom of Y.



(iii) Covalent bond

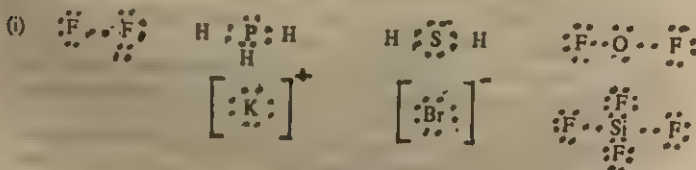
(iv) Carbon tetrachloride

(h) 1. Graphite has a layer structure in which each carbon is sp^2 hybridized. Electrons present in the unhybridized orbital are delocalized and conduct electricity. In diamond, each carbon is sp^3 hybridized and no mobile or delocalized electrons are available.

2. Because of three dimensional network and strong C - C bonds diamond is the hardest

3. In oxygen molecule, there are two unpaired electrons which make it paramagnetic.

4. It is because of hydrogen bonding present in water molecules.



(ii)

K	in group	1
L	in group	14
M	in group	17

(iii)

K and M
 K^+ and M^-



6.6

(i) P in PCl_5 (ii) S in SF_4 ; S in SF_6 ; Be in BeF_2

(iii)

 BeCl_2 — Linear SiF_4 — Tetrahedral AsF_5 — Trigonal bipyramid H_2Se — V—shape HgCl_2 — Linear BF_3 — Tetrahedral SF_4 — See saw shape ClF_3 — T—shape SO_2 — Plane Trigonal SO_4^{2-} — Tetrahedral(iii) SO_2 is a bent molecule. For a linear shape of $\text{O}=\text{S}=\text{O}$ dipole moment is zero as the centre of positive charge and negative charge coincides

(iv) (a) Zero (b) Zero (c) Zero (d) Zero (e) Zero

(v) Sulphur, S_8

Carbon and its Compounds

In her answers, Nature never uses italics. It is upto you to distinguish the important from the trivial.

Oliver Watts

UNIT PREVIEW

- 7.1 Introduction
- 7.2 Elemental carbon
 - 7.2.1 The uniqueness of carbon
 - 7.2.2 Allotropy of carbon
 - 7.2.3 Crystalline allotropes
 - 7.2.4 Amorphous allotropes
- 7.3 Inorganic compounds of carbon
 - 7.3.1 Oxides of carbon
 - 7.3.2 Halides of carbon
 - 7.3.3 Carbides
- 7.4 Tetravalency of carbon and formation of compounds
- 7.5 Impact of organic compounds on mankind
- 7.6 Nomenclature of organic compounds
 - 7.6.1 Hydrocarbons
 - 7.6.2 Characteristic groups (functional groups)
- 7.7 Some common organic compounds and their uses

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Comment on the position of carbon in the periodic table.
2. Have the fair knowledge about the occurrence of carbon.
3. Recognize the various allotropic forms of carbon.
4. Appreciate the tetravalency of carbon.
5. Define the following terms : inorganic chemistry, organic chemistry, catenation, hydrocarbon (saturated and unsaturated), alkane, alkene, alkyne, functional group, general formula, homologous series, homologue, isomer and structural formula.
6. Classify the hydrocarbons.
7. Give the common and IUPAC names of various organic compounds.
8. Write general formulae for the aliphatic hydrocarbons and draw structural formulae for simple aliphatic hydrocarbons and their isomers.
9. Describe some of the oxides, halides and carbides of carbon.
10. Appreciate the impact of organic compounds on mankind.
11. Recognize and name the simple alkyl groups.
12. Give examples and illustrations of the various functional groups listed in this unit.
13. Give common and IUPAC names of some of the lower members of the homologous series of alcohols, aldehydes, carboxylic acids and their functional derivatives, etc.
14. Describe the harmful effects of drinking alcohol.
15. Appreciate the utilization of organic compounds.

7.1 INTRODUCTION

Carbon was known as a substance in prehistory (charcoal, soot) though its recognition as an element came much later. Carbon makes up only about 0.08 percent of the combined lithosphere, hydrosphere and atmosphere and is found in the earth's crust. Oxygen, silicon, aluminium, and iron are much more abundant, but carbon is the basis of life on earth. Although living matter is composed almost entirely of water and an enormous variety of carbon compounds - the nutrients, the building blocks of plants and animal tissues, carbon is only the seventeenth most abundant element. Other carbon compounds like petroleum and petrochemicals are the primary fuels and the raw materials for manufacturing plastics and synthetic fibers.

There are an enormous number of carbon compounds and almost all of them are classified as organic compounds. At one time it was believed that the ability to produce carbon compounds rested exclusively with organic or living matter; hence, these compounds were called organic compounds. Compounds occurring in the nonliving or mineral world were called inorganic compounds. The creation of carbon compounds was thought to be directed by a mysterious, "Vital force" contained in living matter. Vitalism met with a failure in 1928 when Friedrich Wohler, a German chemist, synthesized an organic compound, urea (a biological waste product present in urine) by heating ammonium cyanate, an inorganic compound which is not found in living matter. The synthesis of urea showed that the belief that organic compounds could be made only in living tissue was incorrect.

Since Wohler's day the definition of organic chemistry has been extended to include the study of all carbon compounds, irrespective of their origin but with the exception of CO_2 , carbonates, and a few other compounds traditionally regarded as inorganic compounds.

Organic chemistry is now defined as the chemistry of compounds of carbon. The chemistry of all the other elements and their compounds is called inorganic chemistry. There are more than five million known organic compounds (isolated or synthesized) but only 100,000-200,000 inorganic compounds. Many organic compounds have proved useful as medicines, plastics, paints, fibres, fertilizers, insecticides, perfumes, etc. In this unit, we will explore the immense structural and chemical diversity of carbon compounds.

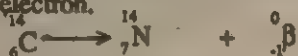
7.2 ELEMENTAL CARBON

Carbon is a typical non-metal. Its electronic arrangement is $1s^2, 2s^2, 2p^4$ with 4 electrons in the valence shell. It is placed in group 14 of the periodic table.

Carbon exhibits allotropy, its chief allotropes being diamond and graphite.

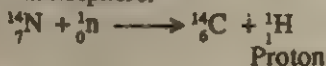
Carbon is abundant in nature and is found in both the free and the combined states. It occurs in the earth's crust in the form of calcium or magnesium carbonate rocks such as calcite, limestone, dolomite, marble and chalk. In the free state it occurs as diamond and graphite in crystalline form, and as coal in amorphous form. In the atmosphere, it occurs as carbon dioxide (combined form) (Carbon dioxide acts as a reservoir for photosynthesis in plants). It is a major constituent of petroleum and natural gas.

Naturally occurring carbon contains two stable isotopes $^{12}_6\text{C}$ (98.9% of natural carbon) and $^{13}_6\text{C}$ (~ 1.1%). The atomic mass unit (amu) is based on the mass of a $^{12}_6\text{C}$ atom as a standard. A third naturally occurring isotope $^{14}_6\text{C}$ is radioactive and decays by emitting a high energy electron.



Beta particle
(High energy electron)

Radioactive carbon $^{14}_6\text{C}$ is continuously formed by the nuclear reactions of neutrons from cosmic rays with nitrogen atoms in the upper atmosphere.



Carbon is one of the most important elements. Its importance for the life process is very great as it is found in all living matter and in all compounds necessary for life such as carbohydrates, proteins, fats, starches, vitamins, oils, etc. Fossil fuels such as lignite, coal and oil which are derived from living matter are all rich in carbon compounds.

7.2.1 The Uniqueness of Carbon

Modern civilization is almost totally dependent on hydrocarbons, which occur in the earth's crust as natural gas and petroleum. There are an enormous number of compounds comprising carbon and hydrogen. Why does carbon have this unique ability to form an enormous number of compounds? There are three distinct characteristics of carbon that enable it to form so many stable compounds.

- (i) Carbon has a fully shared octet of electrons in its compounds.
- (ii) Carbon can form single, double and triple bonds to itself (catenation)
- (iii) Carbon can form four covalent bonds.

7.2.2 Allotropy of Carbon

The phenomenon of existence of different forms of an element is called allotropy.

Carbon occurs in two allotropic forms, viz., crystalline and

amorphous. The crystalline varieties are,

1. Diamond, and 2. Graphite

Whereas amorphous varieties are,

1. Coal, 2. Wood charcoal, 3. Animal charcoal, 4. Sugar charcoal, 5. Lamp black or soot, 6. Coke, and 7. Gas carbon.

Allotropes are forms of the same element differing in the nature of their chemical bonds, in their molecular masses or in their crystal structures.

7.2.3 Crystalline Allotropes

1. **Diamond** : It is one of the hardest natural substances known. When pure, it is colourless, has extremely high melting point and does not conduct heat and electricity. Its specific gravity is 3.52 and refractive index is 2.45.

The high refractive index of diamonds led to their use as jewellery in the very earliest civilization. Black diamonds, unsuitable for gemstones, are used in glass cutters, and in diamond studded saws. The modern industrial uses of diamond, almost all, result from its hardness — drilling, cutting, grinding and for the bearings in precious instruments such as watches. Powdered diamond is used as abrasives for smoothening very hard materials.

Diamond's hardness, high melting point, transparency and its inability to conduct heat and electricity all arise from its crystal structure. The carbon in diamond is tetravalent, each atom being covalently bonded (sp^3 hybrid bonds) to four other carbon atoms in such a manner that the whole crystal is, in fact, one giant molecule (Fig. 6.68)

In diamond, the interlocking network of covalent bonds in three dimensions produces large crystals that are actually single molecules. This makes diamond extremely hard and rigid. Diamond has a more compact structure than graphite (Fig. 6.69) so that high pressure favours its existence and at 2273K and 100,000 atmosphere pressure. It is possible to convert graphite to diamond using transition metal catalysts. The process is used commercially to produce diamonds of industrial quality for use in cutting tools and in solid state electronic devices.

2. **Graphite** : Graphite possesses metallic lustre. It is black, soft and high melting substance. It is a good conductor of heat and electricity and has a slippery and greasy feel. It occurs in nature. It can also be manufactured artificially by heating coke to about 3273K in an electric furnace.

The uses of graphite are related to its conducting and lubricating qualities. Mixed with desired quantities of wax or clay, graphite is used for making lead pencils. The percentage of added clay deter-

mines the hardness of the pencil. It is used as a high temperature lubricant, as inert electrodes in various electric furnaces and electrolytic processes and as a moderator for slowing down neutrons in nuclear reactors.

In graphite, the carbon atoms are arranged in flat, parallel layers (Fig. 6.69, Table 7.1). Within each layer, each carbon atom uses three coplanar sp^2 hybrid orbitals to bond covalently to three others, resulting in a series of interconnecting planar hexagonal rings. The remaining fourth electron is delocalized over the whole layer. This delocalization of electrons imparts to graphite, nature of conducting electricity and shiny appearance. An electron forced into one end of a layer can produce a flow of charge through the electron cloud and can cause an electron to release from the other end. It has been experimentally seen that the electrical conductivity is very good in a direction parallel to the layers, but very poor in a direction perpendicular to the layers.

In the common variety of graphite (i.e., hexagonal) the layers are arranged in the sequence ---- ABAB ---- with carbon atom in alternate layer vertically above each other, whereas in the other form of graphite (or rhombohedral) the stacking sequence is ---- ABC---ABC---. The two forms are interconvertible.

These layers are loosely joined to one another by bonding. It is more like van der Waal's forces than covalent bonding. Because of this the layers can slide over one another easily, and thus, graphite serves as a good lubricant. Gas molecules trapped between the layers also

TABLE 7.1 Physical and chemical properties of graphite and diamond

S.N.	Property	Graphite (black)	Diamond
1.	Colour and appearance	Grayish black, metallic lustre	Colourless, transparent, brilliant
2.	Nature of crystal	Hexagonal, soft and slippery	Tetrahedral, very hard (hardest natural substance)
3.	Specific gravity	2.3	3.52
4.	Refractive index	—	2.45
5.	Purity	90.97% pure	Purest form of carbon (almost 100% pure)
6.	Conductivity	Good conductor of heat and electricity	Bad conductor of heat and electricity
7.	Effect of heat	Burns in air at 973K giving CO_2	Burns in oxygen at 1173K giving CO_2
8.	Solubility	Does not dissolve in ordinary solvents	Does not dissolve in ordinary solvents
9.	Effect of acids and alkalis	Not attacked except by conc. HNO_3 which gives graphitic acid	Not attacked
10.	Reaction with halogens	Forms CF_4 with F_2 at high temp,	Forms CF_4 with F_2 at high temperature

help considerably by acting as a molecular "ball bearing".

Note. The contrasting properties of diamond and graphite arise from the different types of bonding within their respective crystals.

The physical and chemical properties of these are summarized in Table 7.1

7.2.4 Amorphous Allotropes

1. **Coal** : It is formed in nature as a result of the slow decomposition of vegetable matter under the influence of heat, pressure and limited supply of air. Coal is found in various forms which represent the different stages of transformation of vegetable matter. The first stage is peat, the carbon content is about 60%. Next stage is the formation of lignite. It is harder and contains about 67% carbon. Bituminous coal contains about 80% carbon. Anthracite is the last stage of transformation. It contains upto 90% carbon.

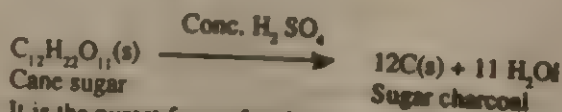
The chief coal mines in India are Bokaro, Jharia, Raniganj and Pench valley. About 98% coal is consumed in the country. Largest consumers are the railways, mills and factories.

2. **Wood charcoal** : It is obtained by heating wood at a high temperature in a limited supply of air. Pieces of wood are arranged in the form of a kiln. The outer surface is pasted with mud. The central region is kept empty for chimney action. It is fired, a part of the wood is burnt and the heat chars the rest to form wood charcoal. Now-a-days wood charcoal is prepared by the destructive distillation of wood in big retorts or trolly furnaces.

Wood charcoal is a soft and porous solid substance with a specific gravity of 1.5. It possesses the property of absorbing coloured and odouriferous gases. Coconut charcoal at the temperature of liquid air is utilized for the separation of rare gases (Dewar's method).

3. **Animal charcoal** : It is prepared by the destructive distillation of bones. It contains about 90% of calcium phosphate. It absorbs colouring matter from liquids. Thus, it is used in sugar industry and in the manufacture of organic liquids. It is also used in decolourizing petroleum jelly.

4. **Sugar charcoal** : It is obtained by the action of concentrated sulphuric acid on cane sugar.



It is the purest form of carbon.

5. **Lamp black** : It is prepared by burning tar, turpentine oil or other vegetable oils in a limited supply of air. It is a soft black powder. It is used in making printing inks, black paints, Indian ink and

boot polishes.

6. **Coke** : When coal is destructively distilled in retorts, vapours are given out which on condensing form coal tar. The residue left behind in the retorts is coke. It is a pure form of carbon. It burns without smoke and is used as a fuel. It is chiefly used as a reducing agent in metallurgy and in making fuel gases.

7. **Gas carbon** : When coal is destructively distilled in retorts, a black mass deposits on the walls and roof of the retorts. Such a deposit is called gas carbon. It is a very pure form of carbon and is very hard. It is a good conductor of electricity and is used in making electrodes.

7.3 INORGANIC COMPOUNDS OF CARBON

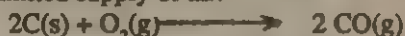
Carbon, the first element in group 14, is a typical non-metal. It is much less reactive than some of the important non-metals such as phosphorus, and halogens. Its reactivity parallels that of nitrogen and sulphur, which are also rather unreactive at ordinary temperatures. Carbon does, however, react with oxygen, strong oxidizing agents (HNO_3 , H_2SO_4 , etc.) many metal oxides, many other elements forming carbides and compounds at high temperatures. It serves as a very useful reducing agent. Carbonates and bicarbonates, the salts of unstable carbonic acid, H_2CO_3 , decompose on heating to form carbon dioxide and water.

7.3.1 Oxides of Carbon

All forms of carbon burn to form oxides. Carbon monoxide, CO and carbon dioxide, CO_2 are the two important oxides.

Carbon Monoxide

Carbon monoxide is formed by burning carbon or a hydrocarbon in a limited supply of air.



Industrially, carbon monoxide mixed with hydrogen is produced on a large scale by passing steam over red hot coke.



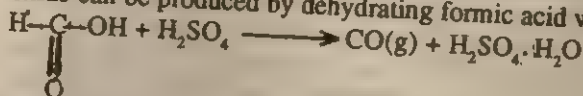
The mixture of carbon monoxide and hydrogen is called **water gas**. It is poisonous due to the presence of carbon monoxide. Its heat value is between those of producer gas and coal gas (a mixture of CH_4 , H_2 and CO).

When air is used in place of steam, another industrially important gas, i.e., producer gas is produced.

Producer gas, a mixture of carbon monoxide and nitrogen, is made by passing air through red-hot coke. The nitrogen present in the air remains unchanged, but oxygen oxidizes carbon to carbon monoxide.



It is poisonous due to the presence of carbon monoxide. It has a low heat value because of its high nitrogen content. Pure carbon monoxide can be produced by dehydrating formic acid with conc. H_2SO_4 .

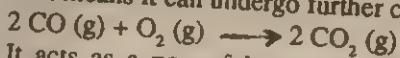


Formic acid

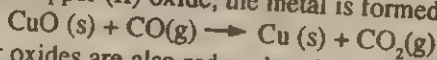
Properties of carbon monoxide

Carbon monoxide is a colourless, odourless and tasteless gas. It is almost insoluble in water.

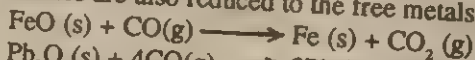
1. Carbon monoxide burns with pale blue flame to form carbon dioxide. It means it can undergo further combustion.



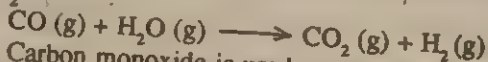
2. It acts as a powerful reducing agent. When it is passed over heated copper (II) oxide, the metal is formed along with CO_2 .



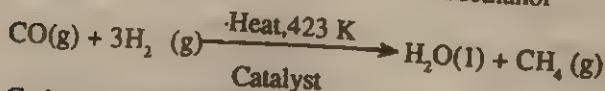
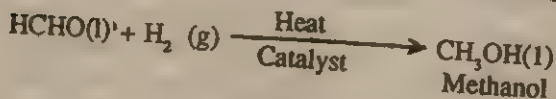
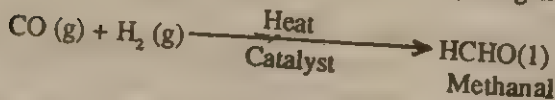
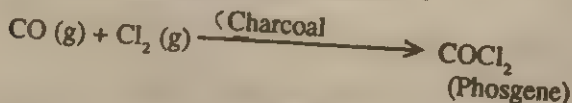
Other oxides are also reduced to the free metals, e.g.,



3. It reduces steam at high temperature giving a mixture of CO_2 and H_2 .



4. Carbon monoxide is used as a starting material for the synthesis of many industrially organic substances, e.g.



Carbon monoxide is poisonous because of its ability to bond strongly to the iron present in the oxygen - carrier protein, haemoglobin in red blood corpuscles, thus, preventing the blood to carry oxygen.

Carbon Dioxide

Carbon dioxide occurs in the atmosphere in very small amounts. Natural processes account for most of the carbon dioxide which tries to maintain equilibrium with CO_2 dissolved in natural waters, that contained in earth's crust (as limestone, CaCO_3), that participating in photosynthesis, and that produced by combustion of fossil fuels.

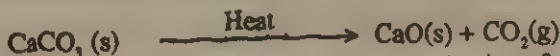
The increasing use of fossil fuels is adding CO_2 to the atmosphere. Carbon dioxide and water present in the atmosphere do not prevent sunlight from reaching the surface of the earth. However, the earth re-radiates some sunlight in the form of infrared radiation which is readily absorbed by both CO_2 and H_2O . As a result, the temperature of atmosphere increases (by $2\text{--}3^\circ\text{C}$). This is called the green house effect. This increase in temperature may help in partial melting of polar ice caps, a rise in the level of the oceans that would submerge some coastal cities and a dramatic change in climates.

Preparation of carbon dioxide

Carbon dioxide is prepared in the laboratory by the action of dilute hydrochloric acid on marble chips (contains CaCO_3) or any other carbonate and bicarbonate.

It is produced commercially as a by-product in :

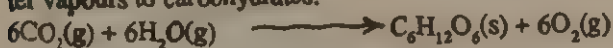
(a) the production of quick lime.



(b) the fermentation of sugar or starch for production of ethyl alcohol.

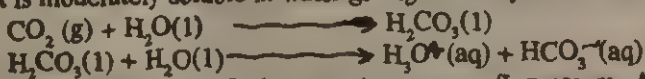


Photosynthesis in plants involves the conversion of CO_2 and water vapours to carbohydrates.



Preparation of carbon dioxide

Carbon dioxide is a linear and non-polar molecule (Unit 6). Carbon dioxide is a colourless, odourless gas. It is heavier than air. It is not poisonous in nature, but still it does not support life in animals and human beings. It stimulates the respiratory centres and is, thus employed with oxygen for revival in cases of drowning and gas poisoning. It is moderately soluble in water giving a weakly acid solution.

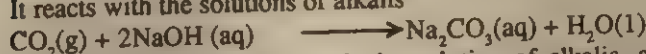


The solubility of CO_2 in water increases with pressure. A saturated solution of carbon dioxide at 8 atm pressure is known as soda water. Other aerated soft drinks are also solutions of carbon dioxide (as well as flavouring and colouring substances) in water under pressure.

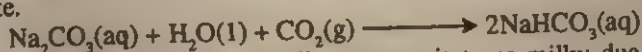
Carbonic acid is a weak dibasic acid which forms two sets of salts, the hydrogen carbonate, HCO_3^- and carbonates CO_3^{2-} . In solution, alkali metal carbonates and bicarbonates behave alkaline due to hydrolysis.



2. It reacts with the solutions of alkalis



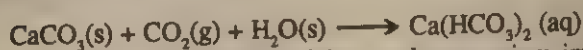
When CO_2 is bubbled through the solution of alkalis, sodium carbonate is formed, but continued supply of gas produces the bicarbonate.



3. On passing CO_2 through lime water, it turns milky due to the formation of insoluble CaCO_3 .

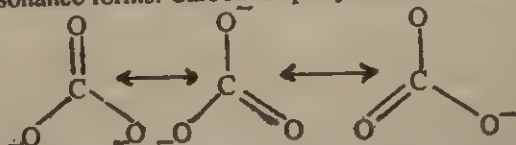


More of carbon dioxide converts CaCO_3 into soluble bicarbonate salt.



Soluble bicarbonates of calcium and magnesium impart temporary hardness to water. Of the common carbonates only those of sodium, potassium and ammonium are soluble in water. All bicarbonates are soluble in water.

Carbonate ion is symmetrical and trigonal planar and is shown by three resonance forms. Carbon is sp^2 hybridized.



Many carbonates like $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (washing soda) K_2CO_3 , CaCO_3 and NaHCO_3 (baking soda) are industrially and commercially useful chemicals. Their chemistry will be discussed in Unit 14.

Carbon dioxide is well known in its solid form as **dry ice**. It is obtained by cooling CO_2 under pressure. Above 195K , it sublimates without liquefying (hence, dry ice). Solid CO_2 is used as a refrigerant in food industry. Pop singers sometimes like to enhance their performance by taking lumps of dry ice. As it sublimates, it cools the moist air and swirling clouds of water droplets form. Carbon dioxide gas is used in controlling the fire. Fire extinguishers work on the utilization of it.

Some of the physical properties of carbon monoxide and carbon dioxide are listed in Table 7.2.

TABLE 7.2 : Some physical properties of CO and CO₂

Property	CO	CO ₂
M.P.(K)	68	216. 4 (52 atm)
B.P.(K)	81.5	194..5 (sublimes)
Hf (kJ mol ⁻¹)	-110.5	-393.5
Density (g/cm ³) at 298 K	1.250	1.977
Bond length, C—O (pm)	112.8	116.3

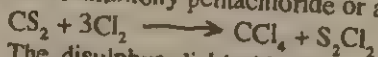
7.3.2 Halides Of Carbon

All the four possible halides of carbon are known (CF₄, CCl₄, CBr₄ and CI₄). Their physical properties are listed in Table 7.3.

TABLE 7.3 : Properties of halides of carbon

Property	CF ₄	CCl ₄	CBr ₄	CI ₄
Melting point (K)	884	250.7	366.7	444
Boiling point (K)	145	349.4	decomposes	decomposes
Bond energy C—X (kJ mol ⁻¹)	515	295	235	—
Density (g/cm ³)	1.96	1.594	2.961	432
Properties	Stable gas	Stable colourless liquid	Yellow solid, decomposes on heating	Red solid, decomposes readily by heat or light

All carbon tetrahalides are prepared by prolonged halogenation of hydrocarbons. Carbon tetrachloride is an important solvent. It is prepared by passing chlorine gas through hot carbon disulphide in the presence of antimony pentachloride or aluminium chloride catalyst.



The disulphur dichloride is separated by fractional distillation. Stability of the tetrahalides decreases from CF₄ to CI₄.

Fluorocarbons

Controlled reactions of fluorine diluted with argon or nitrogen with hydrocarbons in the presence of copper fluoride give an interesting series of compounds. These fluorides of carbon are called fluoro-carbons. They can also be conveniently prepared by passing hydrocarbons over cobaltic fluoride at 423-473K. Mixed chloro-fluoro-compounds (chloro compounds) can also be prepared by reaction between CCl₄ and SbF₃.

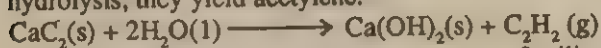
Fluorocarbons are inert, stable and inflammable. They are used as lubricants, refrigerants, freezers, hydraulic liquids, plastics and insecticides, paints and also as propellant gases in pressurized spray cans for

hair sprays. Teflon, a fluorocarbon polymer, is very tough, high melting and chemically inert plastic material. It is used in making greaseless cook-ware, bearings and valves which require no lubrication and containers for corrosive chemicals. The mixed chloro-fluoro-compounds are known as 'Freons'. Freon-12 (CCl_2F_2) is widely used as a refrigerant (volatile, non-toxic and non-corrosive). CCl_3F is used as an insecticide.

7.3.3 Carbides

Binary compounds of carbon with elements which are more electropositive than carbon or whose electronegativity is less than carbon (i.e. less than 2.5) are termed carbides. There are three main types : (a) salt-like, (b) interstitial, and (c) covalent. Carbides are generally prepared by the direct union of the elements, by heating an oxide with carbon or by heating a metal in the vapours of a hydrocarbon.

Salt-like or ionic carbides : These carbides usually contain the ion C^{2-} and they are formed by the alkali and alkaline earth metals and also by certain low electropositive metals such as Zn and Be. On hydrolysis, they yield acetylene.



Calcium cyanamide finds its use as fertilizer. It is obtained when CaC_2 reacts with nitrogen. There are some carbides which contain C^{4-} . Beryllium carbide Be_2C and aluminium carbide Al_4C_3 belong to this class of carbides. They yield methane on hydrolysis.

Interstitial carbides : These carbides are formed by transition metals, the carbon atoms occupying octahedral sites in the metal lattice. They are very hard and brittle, e.g., tungsten carbide, (WC). This type includes, TiC , ZrC , MoC , etc. These carbides are not attacked by water or dilute acids, have high melting points (3300—3800K), are extremely hard, lustrous and good electrical conductors. There is another type of carbides which are also covered under this category. This class arises when the cavities in the metallic lattice are not large enough to hold a carbon atom. The carbon atoms, in the form of chains, run through a very distorted metallic lattice. Carbides of these types hydrolyze to give a variety of hydrocarbons.

Covalent carbides : The carbides of certain non - metals acquire a network of covalent bonds and become giant molecules. Carborundum (SiC) and boron carbide (B_4C_3) belong to this class. Both are hard, infusible and inert. Carborundum is an infinite three dimensionally array of four coordinated silicon and carbon. It is used as an abrasive. Boron carbide involves icosahedral B_{12} units linked by linear C_3 chains.

7.4 TETRACOVALENCY OF CARBON AND FORMATION OF COMPOUNDS

Carbon is the first member of group 14 of the periodic table. All the group 14 elements have four electrons in the valence shell. Among these carbon is the lightest and unique.

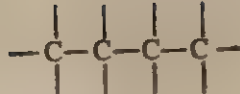
It is difficult for carbon either to lose valence electrons or gain electrons in the valence shell and form ions. This is because it would need a large amount of energy. Carbon, therefore, invariably forms covalent bonds by sharing its four valence electrons with itself or with other elements. Thus, carbon forms compounds with four covalent bonds. Carbon can form these bonds according to any one of the combinations shown in Table 7.4. A long dash (—) indicates a bond consisting of a shared pair of electrons, one from the carbon atom and second from another atom. Carbon, with its four outer electrons and shared electrons from each of the four bonds in a compound has a complete outer level of eight electrons (octet). Thus, carbon has a covalency of four, *i.e.*, it is tetravalent in nature.

TABLE 7.4 The possible bonding arrangement of a carbon atom

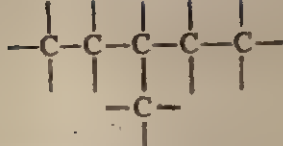
Arrangement	Description	Total number of bonds
$\begin{array}{c} \\ \text{---C---} \\ \end{array}$	4 single bonds	4
$\begin{array}{c} \text{---C=} \\ \end{array}$	2 single bonds	4
$\begin{array}{c} \text{=C=} \end{array}$	1 double bond	4
	2 double bonds	
$\text{---C}\equiv$	1 single bond	4
	1 triple bond	

Further on the basis of qualitative and quantitative analysis of several organic compounds, Lavoisier established that carbon along with a few other elements is contained in all the organic compounds. His work was supported by Kolbe, Kekule and Berthlot. Their painstaking work led them to conclude that organic compounds could generally contain oxygen, nitrogen, sulphur, and halogens along with carbon and hydrogen.

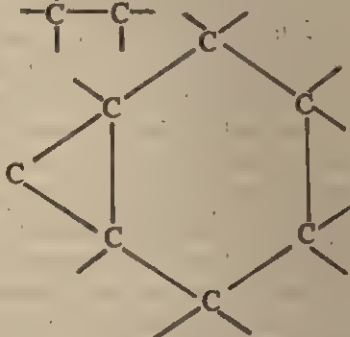
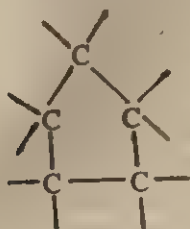
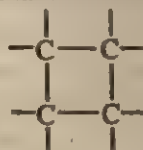
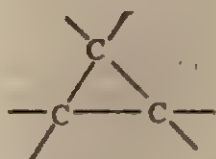
Carbon forms several million different compounds. This number is greater than the number of compounds formed by any other element. One reason for the large number of organic compounds is that carbon atom has a unique tendency to form long chains of carbon atoms (Section 7.2.1). This tendency to form bonds with itself leads to the formation of compounds that consists of two types of chains. These are (i) open chains, and (ii) closed chains or ring type chains.



Open chain
(Straight chain)



Open chain
(Branched chain)



Closed chains
Ring type chains

Bond energy data (Table 7.5) show that carbon-carbon bonds are stronger than bonds between like atoms formed by the other members of the group. Carbon has a unique tendency to form long chains of carbon atoms (catenation). Numerous carbon compounds are known in which two or more carbon atoms are covalently bound together. Molecules with chains of upto six silicon atoms have been made, catenation almost disappears with the remaining elements. Silicon forms much stronger bonds with fluorine, oxygen and chlorine than with itself or hydrogen (Table 7.5) and in contrast to the hydrocarbons, the silicon compounds which contain Si-Si or Si-H bonds are generally very reactive, *e.g.*, hydrides of silicon, silanes.

TABLE 7.5 Bond energies involving group 14 elements

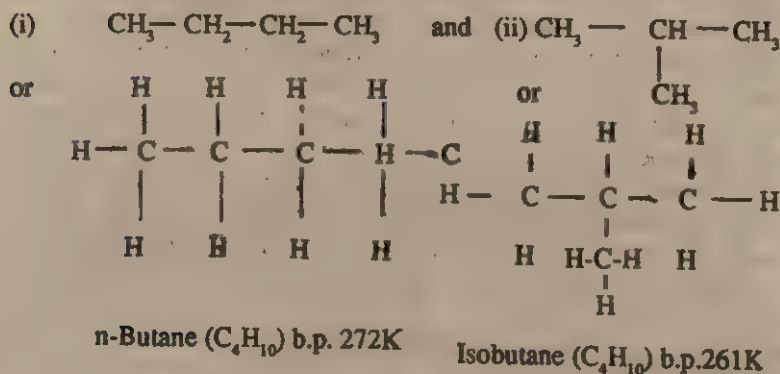
Bond	Energy (kJ mol ⁻¹)	Bond	Energy (kJ mol ⁻¹)	Bond	Energy (kJ mol ⁻¹)
C—C	356	Si—Si	226	Ge—Ge	188
C=C	608				
C≡C	820	Si—H	318	Sn—Sn	150
C—H	414	Si—O	464		
C—O	360	Si—F	598		
C—F	489				

The following typical conclusions may be drawn from the energy values given in the Table 7.5

1. the high bond energy of H-H bond agrees with the unreactivity of the hydrocarbons.
2. the very high bond energy of the C-F bonds accounts the inertness of the fluorocarbons.
3. the high bond energy of Si-O bond explains the abundance of compounds containing Si-O bonds (silica and silicates) in nature.
4. the increase in bond order results in increase in bond strength, and therefore, increase in bond energy.
5. The strength of C-H and C-C bonds and the ability of C to form multiple bonds with itself (also with oxygen and nitrogen) which are responsible for the extent of organic chemistry.

The extent of organic chemistry is also attributed to the phenomenon of isomerism shown by organic compounds.

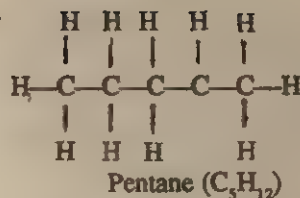
The compounds having the same molecular formula but different structural formulae are known as isomers. These isomers have different properties (b.p., m.p., densities, etc.). This phenomenon, in which different compounds exist with the same molecular formula but different structural formulae, is called isomerism. For example, the formula C_4H_{10} represents two different compounds.



We find that both n-butane and isobutane have the same molecular formula, C_4H_{10} , but different structural formulae, therefore, butane (b.p. 272K) and isobutane (b.p. 261K) are isomers.

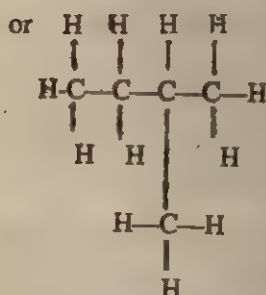
Formula C_5H_{12} represents three isomers, : pentane, isopentane and neopentane.

(i) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$ (ii) or



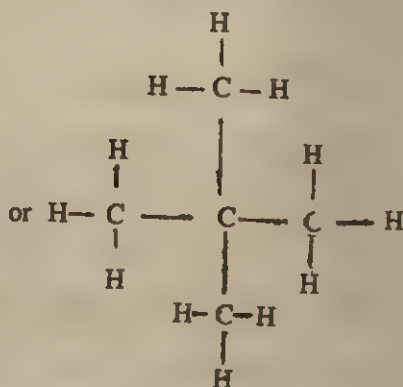
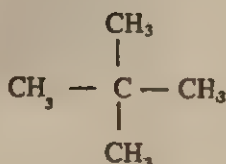
(ii) $\text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_3$

CH_3



Isopentane (C_5H_{12})

(iii)



Neopentane (C_5H_{12})

Sources of Organic compounds

The organic compounds can be obtained from natural sources and by synthetic processes. Natural sources are of four types : (i) micro-organisms, (ii) plant kingdom, (iii) animal kingdom, and (iv) mineral kingdom.

(i) **Micro-organisms** : These are responsible for products obtained from fermentation processes.

(ii) **Plant kingdom** : Maximum number of organic compounds such as starch, sugar, cellulose, vegetable oils, essential oils, drugs, dyes, insecticides, alkaloids, gums, perfumes, etc., are obtained

from plants.

(iii) **Animal kingdom** : Fats, urea, honey, hormones, vitamins, proteins, etc., are directly obtained from animals.

(iv) **Mineral kingdom** : Coal is a rich source for synthetic products like benzene, toluene, phenol, naphthalene, etc. Petroleum is another important source of organic compounds. Petrol, kerosene, lubricating oil, vaseline and other petrochemicals are obtained from petroleum.

A large number of organic compounds are obtained in the laboratory by synthetic processes. A chemical which is obtained from petroleum or natural gas is a derivative of petroleum product, and is known as **petro-chemical**.

TABLE 7.6 : Distinction of organic compounds from inorganic compounds

Property	Organic compounds	Inorganic compounds
1. Abundance	Enormous in number	Limited in number
2. Nature or bonding	Involve covalent bonding	Involve mostly ionic bonding. Also involve covalent bonding
3. Bond formation	Slow	Fast
4. Functional groups	Present	Absent
5. Study of the compounds	Easy to classify into families based upon functional groups	Classification is possible but study is not very convenient.
6. Source	From living matter and synthetic source	Non-living matter associated with mineral world, also synthetic
7. Specificity	Very nearly all organic compounds contain C and H	Can contain any elements.

7.5 IMPACT OF ORGANIC COMPOUNDS ON MANKIND

The chemical profession has contributed much to the progress of civilization. We have moved through the centuries from the art and magic of the alchemists to the very different objectives and methods of modern chemistry, but there is a debt to be acknowledged. Our ancestors devoted their resources and energies fruitlessly to the creation of a mythical substance, the Philosopher's stone (Paras). It was believed that this stone could change the common metals it touched into gold. They also tried to discover the 'Elixir of Life' that would assure eternal youth. This dream too has never been achieved. Despite their failures, science had its raw beginning in their arcane laboratories.

Chemistry has contributed significantly to our material comfort. But there is much left to do. Think of areas in which the beauty of chemistry is apparent in controlling population explosion and environmental pollution, in fighting against hunger and disease, in providing new energy sources, in providing synthetic fibres, in making national economy strong, etc.

All living systems derive their energy from organic compounds such as carbohydrates and fats and grow using amino acids and proteins. Carbohydrates are among the most common constituents of plants and animals. In animals they provide a source of energy, while in plants they form the greater part of the cell tissue on which the plant relies for its support. They include familiar substances like glucose, sucrose, starch, cellulose, etc. They provide all the three basic needs of life, viz., food (as starch containing grains), clothing and shelter (cellulose in the form of cotton, linen, wood etc.).

Proteins in life provide protection as skin, hair and nails and motive power as muscles. As enzymes, or organic catalysts, they sustain life by speeding up otherwise slow chemical reactions. They are macromolecules, gigantic polymer of amino acids with high molecular weights produced in plants and animals. They are considered to be the building units of all vegetable and animal bodies. Proteins are essential part of diet and are vital for the maintenance and growth of life.

Nucleic acids (made of carbohydrates) are a class of compounds which are important for the growth and development of all forms of life and for the transmission of hereditary characteristics from one cell to another.

Vitamins are a group of biocatalysts 'vital' for life. They are required by the body in small quantities to maintain normal health and growth. However, these must be supplied through diet or as 'vitamin preparations' as these cannot be synthesized by the body. Their deficiency leads to a number of diseases.

Hormones constitute a group of biomolecules that have an important role in regulating many metabolic processes and sex characteristics. They are produced by ductless glands and secreted directly into the blood stream. A disturbance in hormonal balance may lead to abnormal metabolic processes.

Nucleic acids, vitamins and hormones are all organic compounds.

Natural fibers like cotton, wool or silk and synthetic fibers like, nylon, rayon, polyester are the gifts of organic chemistry.

Perhaps the biggest impact of organic chemistry in mankind has been in the understanding, prevention and cure of diseases. This has enabled man to live a longer and healthier life. Anaesthetics and anal-

gesics make modern surgery possible. Chemists have developed disease curing and life saving drugs like - sulphur drugs, antimalarial (quinine, chloroquine, etc.) and antibiotics (streptomycin, penicillin, etc.).

Through the use of organic compounds, such as fertilizers (urea) and pesticides (DDT, malathion, gammexane) fungicides (chloranil) and weed killer (2, 4D) drastic agriculture reforms have been possible. These have been able to help us controlling the constant strains on our food resources because of increasing population.

Among our various major fuels and energy sources, fossil fuels like coal, lignite, petroleum and natural gas are of organic origin. The crude oil is a rich source of different grades of fuels (for automobiles, aeroplanes and domestic use) and a vast number of useful chemicals. These chemicals, called as petrochemicals, are used in chemical industries like plastic, resin, synthetic rubber, synthetic fibers, detergents and explosives.

Domestic gas (LPG — liquefied paraffin gas) an important modern fuel, has made cooking very easy. These days gas from animal's waste, gobar gas, is being made available, again through research and development in chemistry.

The other areas wherein organic chemistry also play a vital role are, production of polymers (natural and synthetic - like wood, rubber, paper and plastics), dyes and drugs, soaps and detergents, etc.

Thus, organic chemistry has become an integral part of our culture and consequently is related to many of the issues of our daily lives.

7.6 NOMENCLATURE OF ORGANIC COMPOUNDS

Like any living language, the language of science is constantly changing. The naming of individual compounds and of classes of related compounds has been an important but somewhat controversial subject during the development of chemistry. Many organic compounds isolated from nature were named after their origin for example, penicillin from the word *penicillium notatum*. Acetic acid known for long time was named from the Latin word 'acetum' for "sour wine or vinegar". With the enormous and ever increasing number of organic compounds, it was felt necessary to devise a systematic way of naming them so that their formulae and their structures could be deduced from their names.

The most complete and useful system was evolved during several international conferences ; it is known as the IUPAC (International Union of Pure and Applied Chemistry) system. We will show the rules covering the system in the following pages.

Many organic compounds are still known by their common names. Though these names bear no relation to the IUPAC name or the molecular structure of the compounds. In most cases, common names are simpler than IUPAC names. We will use IUPAC names in this book. However, common names, widely acceptable today, will also be used.

7.6.1 Hydrocarbons

Compounds containing carbon and hydrogen are called **hydrocarbons**. The naming of hydrocarbons is very important because their names form the basis of naming all other organic compounds.

Methane (CH_4), ethane (C_2H_6), propane (C_3H_8), ethylene (C_2H_4), acetylene (C_2H_2), benzene (C_6H_6), etc. are some of the examples of hydrocarbons. Methane, ethane, ethylene, acetylene are aliphatic hydrocarbons whereas benzene is called an aromatic hydrocarbon.

A hydrocarbon is said to be saturated if each carbon atom is bonded to four other atoms by single covalent bonds; no double or triple bonds are present between carbon atoms. Saturated hydrocarbons are non-reactive. Hence, saturated hydrocarbons were earlier also called paraffins (para = less; affins = affinity). The systematic IUPAC name for such compounds is 'Alkanes'. The general formula of alkanes is $\text{C}_n\text{H}_{2n+2}$.

Unsaturated hydrocarbons are those which contain at least one carbon-carbon double or triple bond. According to IUPAC system, hydrocarbons containing at least one ' —C=C— ' bond are called '**Alkenes**' and with at least one ' $\text{—C}\equiv\text{C—}$ ' are called '**Alkynes**'. Thus, alkenes and alkynes are hydrocarbons that contain double or triple bonds. An alkene (or olefin) contains a double bond between two carbon atoms. Their double or triple bonds allow other molecules to be added to the hydrocarbon chain through a reaction. For example, both an alkene and an alkyne can be converted to the corresponding alkane by an addition reaction with H_2 . This reaction is called **hydrogenation**.

The general formula of alkenes is C_nH_{2n} ; the number of hydrogen atoms is twice the number of carbon atoms in the molecule. In case of alkyne family, the general formula is $\text{C}_n\text{H}_{2n-2}$. The formula shows that the number of hydrogen atoms is two less than twice the number of carbon atoms.

Hydrocarbons are classified into three categories depending on the arrangement of carbon atoms.

1. Straight chain hydrocarbons
2. Branched chain hydrocarbons
3. Cyclic hydrocarbons

Naming of Alkanes (also Alkenes and Alkynes) - Continuous and Straight Chain Compounds

These alkanes contain straight chain of carbon atoms. Their names are entirely based upon their straight chain of carbon atoms. The names of such compounds end with 'ane' and carry a prefix depicting the number of carbon atoms present in the chain (except from CH_4 to C_4H_{10} where the prefixes are derived from their trivial or common names.) The prefixes meth-, eth-, prop-, but-, pent-, hex-, hept-, oct-, etc., are used for compounds containing 1, 2, 3, 4, 5, 6, 7, 8, etc. carbon atoms respectively. A list of names of alkanes containing carbons 1-10 is given below (Table 7.7). Their condensed structural formulae are also given.

TABLE 7.7 : Simple alkanes

Name	Molecular formula	Condensed structural formula
Methane	CH_4	CH_4
Ethane	C_2H_6	CH_3CH_3
Propane	C_3H_8	$\text{CH}_3\text{CH}_2\text{CH}_3$
Butane	C_4H_{10}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3^*$
Pentane	C_5H_{12}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3^*$
Hexane	C_6H_{14}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3^*$
Heptane	C_7H_{16}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3^*$
Octane	C_8H_{18}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3^*$
Nonane	C_9H_{20}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3^*$
Decane	$\text{C}_{10}\text{H}_{22}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3^*$

* One of several possible isomers.

Members of the alkene family with their condensed structural formulae are listed in Table 7.8. They all have one double bond between two carbon atoms. The simplest alkene is ethene C_2H_4 which is commonly called ethylene. All the names of the alkenes end in "ene".

Alkynes are hydrocarbons that contain a triple bond between two carbon atoms. The simplest alkyne is ethyne, C_2H_2 , which is commonly called acetylene. Members of the alkyne family with their condensed structural formulae are listed in Table 7.9. The names of all alkynes end in "yne".

TABLE 7.8 Simple alkenes

Molecular formula	Name	Condensed structural formula
C_2H_4	Ethene (ethylene)	$CH_2=CH_2$
C_3H_6	Propene (Propylene)	$CH_2=CHCH_3$
C_4H_8	Butene (butylene)	$CH_2=CHCH_2CH_3^*$
C_5H_{10}	Pentene	$CH_2=CHCH_2CH_2CH_3^*$
C_6H_{12}	Hexene	$CH_2=CHCH_2CH_2CH_2CH_3^*$

* One of several possible isomers

TABLE 7.9 Simple alkynes

Molecular formula	Name	Condensed structural formula
C_2H_2	Ethyne (acetylene)	$HC\equiv CH$
C_3H_4	Propyne (methyl acetylene)	$CH_3-C\equiv CH$
C_4H_6	2-Butyne (dimethyl acetylene)	$CH_3-C\equiv C-CH_3$
C_5H_8	2-Pentyne (ethyl methyl acetylene)	$CH_3-CH_2-C\equiv C-CH_3$

Some properties of individual straight chain alkanes are tabulated in Table 7.10.

TABLE 7.10 Physical properties of straight chain alkanes

Molecular formula	IUPAC name	State at 298 K	Boiling point, K	Melting point, K	Density g/cm ³
CH_4	Methane	gas	112	90	0.424
C_2H_6	Ethane	gas	184	101	0.546
C_3H_8	Propane	gas	231	85	0.501
C_4H_{10}	Butane	gas	273	138	0.579
C_5H_{12}	Pentane	liquid	309	143	0.626
C_6H_{14}	Hexane	liquid	342	178	0.657
C_7H_{16}	Heptane	liquid	371	182	0.684
C_8H_{18}	Octane	liquid	399	216	0.703
C_9H_{20}	Nonane	liquid	424	219	0.718
$C_{10}H_{22}$	Decane	liquid	447	243	0.730
$C_{20}H_{42}$	Eicosane	solid	617	310	0.785

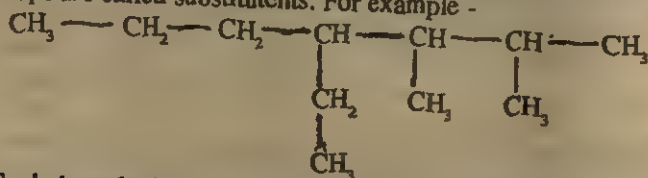
A compound can be represented by its electronic, molecular, structural and condensed structural formulae. Thus, in the case of methane, ethane and propane we have the following :

Hydrocarbon	Molecular formula	Electronic Formula	Structural Formula (graphic)	Condensed structural formula
Methane	CH ₄	$ \begin{array}{c} \text{H} \\ \times \\ \text{H} \times \text{C} \times \text{H} \\ \times \\ \text{H} \end{array} $	$ \begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array} $	CH ₄
Ethane	C ₂ H ₆	$ \begin{array}{c} \text{H} \quad \text{H} \\ \times \quad \times \\ \text{H} \times \text{C} - \text{C} \times \text{H} \\ \times \quad \times \\ \text{H} \quad \text{H} \end{array} $	$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array} $	H ₃ C—CH ₃
Propane	C ₃ H ₈	$ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \times \quad \times \quad \times \\ \text{H} \times \text{C} - \text{C} - \text{C} \times \text{H} \\ \times \quad \times \quad \times \\ \text{H} \quad \text{H} \quad \text{H} \end{array} $	$ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array} $	H ₃ C—CH ₂ —CH ₃

Condensed structural formula is most commonly used.

Branched Chain Compounds

In branch chain compounds, all the carbon atoms are not present in a linear fashion. Some of them are attached to the parent continuous chain at one or more points. This is because hydrocarbon groups can substitute for hydrogen on the parent chain, the substituting hydrocarbon groups are called substituents. For example -



Such branched chain compounds (or hydrocarbons) cannot be named on the basis of number of carbon atoms present in molecular formula of the compound. To facilitate the naming of the compound, the substituent group attached to the parent chain are named by replacing the ending 'ane' of the alkane by 'yl', e.g., methyl for methane. Hence, the substituent groups are called **alkyl groups**. Their general formula is C_nH_{2n+1}. The symbol R is often used to represent a general alkyl group. The possibility of having branched chain alkanes that are structural isomers of the continuous chain alkanes begin with butanes (n = 4).

Some examples of alkyl groups are listed below in Table 7.11

TABLE 7.11 List of alkyl groups

Hydrocarbon		Alkyl group	
Molecular formula	Name	Molecular formula	Name
CH_4	Methane	CH_3-	Methyl
C_2H_6	Ethane	C_2H_5-	Ethyl
C_4H_{10}	Butane	C_4H_9-	Butyl
C_6H_{14}	Hexane	$\text{C}_6\text{H}_{13}-$	Hexyl
$\text{C}_{10}\text{H}_{22}$	Decane	$\text{C}_{10}\text{H}_{21}-$	Decyl
C_6H_6	Benzene	C_6H_5-	Aryl (phenyl)

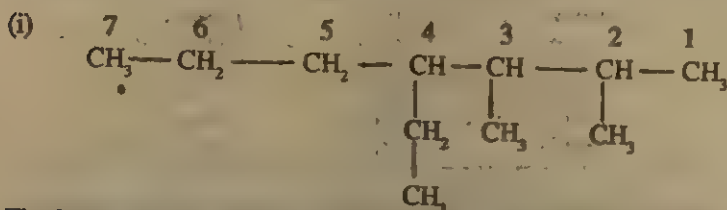
There are names for alkyl groups besides those of methyl, ethyl and propyl mentioned in the Table 7.11. Table 7.12 includes some of these groups.

TABLE 7.12 Names of some common alkyl groups

Name	Alkyl group	Comments
Isopropyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} \\ \\ \text{H} \end{array}$	The prefix <i>iso</i> -is used for carbon chains that are continuous (except for the presence of a methyl group on the carbon second from the unsubstituted end of the longest chains)
Isobutyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{CH} - \text{CH}_2 - \end{array}$ <p>Primary carbon</p>	The carbon joining this alkyl group to another group is bonded to one other carbon; it is a primary carbon
Secondary butyl (<i>sec</i> -butyl)	$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_3 \\ \\ \text{H} \end{array}$ <p>secondary carbon</p>	The carbon joining this alkyl group to another group is bonded to two other carbons; it is secondary carbon.
Tertiary butyl (<i>tert</i> -butyl)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ <p>tertiary carbon</p>	The carbon joining this alkyl group to another group is bonded to three carbons; it is tertiary carbon.
Vinyl	$\begin{array}{c} \text{H} \\ \diagdown \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$	When used as an alkyl group in giving compounds common names, this group, derived from ethene, is called vinyl

The rules for the systematic naming of hydrocarbons are as follows :

1. Select the longest unbranched chain of carbon atoms as the parent chain. This chain is used as the parent structure. Consider the chain.



The longest continuous chain contains seven carbons, so the structure of parent hydrocarbon should be named as heptane.

2. Name the substituent groups. Substituent groups attached to the parent chain are called side chains.

3. Number the carbon atoms in the parent chain starting from the end that will give the substituent groups attached to the chain the smallest numbers. Thus, numbers will depict the positions of the substituent groups on the chain. These numbers become prefixes to the name of the parent alkane. In the example, the substituents and positions are 2-methyl, 3-methyl and 4-ethyl.

4. If more than one substituent groups of the same type are present prefixes : di (2), tri (3), tetra (4), penta (5), etc. are used to indicate their number. But the position of each substituent is indicated by a separate numeral. If different substituents are present they are named in alphabetical order. For purposes of alphabetizing, the prefixes di, tri, etc. are ignored. The present example has two methyl groups. Their correct positions will be : 2, 3-dimethyl.

5. Proper punctuation is very important in naming the organic compounds in the IUPAC system. Commas are used to separate numbers; hyphens are used to separate numbers and words. The name of the hydrocarbon is written as one word.

According to the IUPAC rules, the name of the compound chosen to explain the system will be 4-ethyl-2, 3-dimethylheptane. From this name, with a knowledge of IUPAC rules, it is very easy to give the structural formula of the alkane.

Now to name the hydrocarbons that contain multiple bonds consider the examples,

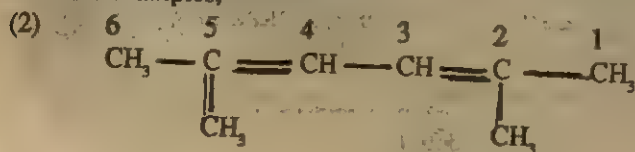
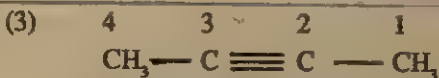


TABLE 7.13 Some important functional groups

Class of Compounds (functional group)	Structure the functional group	IUPAC suffix(s)* or prefix(p)	Example Name * Formula
Alkane	—	—ane(s)	Butane $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
Alkene	$\text{C}=\text{C}$	—ene(s)	1-Butene $\text{CH}_2=\text{CHCH}_2\text{CH}_3$
Alkyne	$\text{C}\equiv\text{C}$	—yne(s)	1-Butyne $\text{CH}\equiv\text{CCH}_2\text{CH}_3$
Arene	—	—ene(s)	Benzene C_6H_6
Alcohol	$-\text{OH}$	'e' of alkane is replaced by -ol(s)	2-Butanol $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
Ether	$-\text{C}-\text{O}-\text{C}-$	—	Ethoxyethane or Diethyl ether $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
Aldehyde	$-\text{C}(=\text{O})\text{H}$	'e' of alkane is replaced by -al(s)	1-Butanal $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$
Ketone	$-\text{C}(=\text{O})-$	'e' of alkane is replaced by -one(s)	2-Butanone $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_3$
Halide	$-\text{X}$ ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$)	Halogeno(p) or ane of alkane is replaced by -yl halide(s)	1-Bromobutane or n-Butyl bromide $\text{CH}_3(\text{CH}_2)_3\text{Br}$
Nitro	$-\text{NO}_2$	Nitro-(p)	1-Nitrobutane $\text{CH}_3(\text{CH}_2)_3\text{NO}_2$
Amine	$-\text{NH}_2, -\text{NH}-, -\text{N}-$	Amino-(p) or -amino(s)	2-Aminobutane or 2-Butanamine $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{CH}_3$
Carboxylic acid	$-\text{C}(=\text{O})\text{OH}$	'e' of alkane is replaced by -oic acid(s)	Butanoic acid $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
Carboxylate ion	$-\text{C}(=\text{O})\text{O}^-$	-oate(s)	Sodium butanoate $\text{CH}_3\text{CH}_2\text{CH}_2\text{COONa}^+$
Acid anhydride	$-\text{C}(=\text{O})\text{O}-\text{C}(=\text{O})-$	-oic anhydride(s)	Butanoic anhydride $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{O}-\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_3$
Amide	$-\text{C}(=\text{O})\text{NH}_2, -\text{C}(=\text{O})\text{NHR}, -\text{C}(=\text{O})\text{NR}_2$	-amide(s)	Butanamide $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$
Acyl halide	$\text{O}=\text{C}-\text{X}$	-oyl halide(s)	Butanoyl chloride $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCl}$

*The suffix or prefix is attached to the corresponding parent saturated hydrocarbon.



6. In alkenes and alkynes, the carbon atoms are numbered so as to give the lowest possible number to the first carbon of the multiple bond. The suffix 'ene' and 'yne' are used to characterise the double and triple bonds respectively. When compounds contain more than one $\text{C} = \text{C}$ bond, a numerical prefix (di, tri, etc.) is used before the 'ene' suffix. This applies to alkynes also.

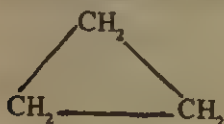
Thus, the names of the hydrocarbons 2, and 3 chosen to explain the system will be,

(2) 2,5 — dimethyl - 2, 4-hexadiene

(3) 2 - Butyne

Another rule is essential for cyclic hydrocarbons.

7. A cyclic compound is named by adding a prefix 'cyclo' to the name of the corresponding straight chain hydrocarbon, e.g.,

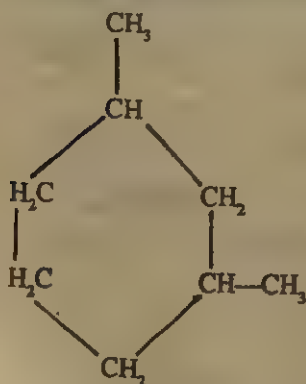


Cyclopropane



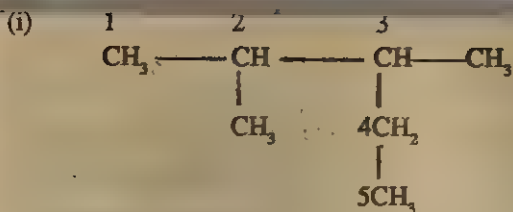
Cyclobutane

The carbon atoms are numbered around the ring so as to give the lowest numbers for the substituent positions. For example,

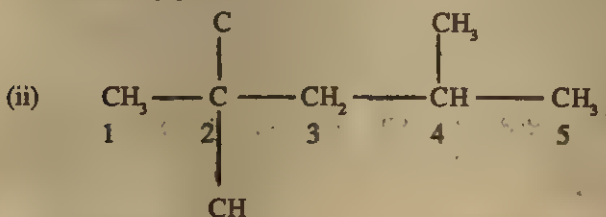


1, 3 - Dimethylcyclohexane

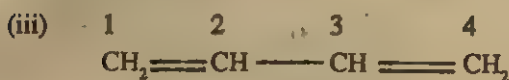
The following examples with their IUPAC names will make the rules further clear.



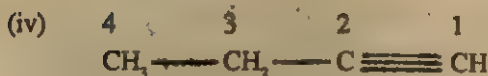
2, 3 - Dimethylpentane



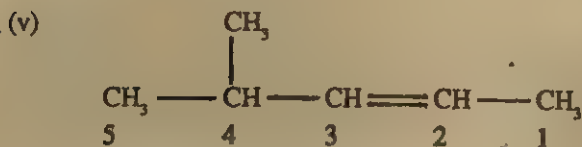
2, 2, 4-Trimethylpentane



1, 3-Butadiene



1-Butyne



4-Methyl - 2- pentene

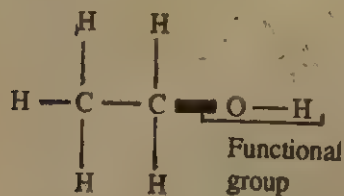
7.6.2 Characteristic Groups (Functional Groups)

Saturated hydrocarbons are quite unreactive, but if one of the hydrogen atoms in saturated hydrocarbons is replaced by another atom or a group of atoms it becomes very reactive. This atom or a group of

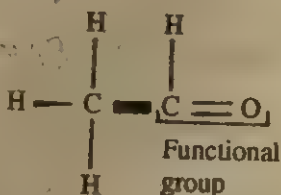
atoms in a molecule that gives the molecule its characteristic chemical properties is called a **functional group**. Several important functional groups are listed in Table 7.13.

These groups cannot exist by themselves but are bonded to alkyl group. The long and thick dashes in the structural formulae of these functional groups show the location of bonding. The functional groups of compounds like those of alcohols, aldehydes and carboxylic acids form bonds with only one alkyl group. Functional groups of other compounds like ethers, ketones and esters form bonds with two alkyl groups.

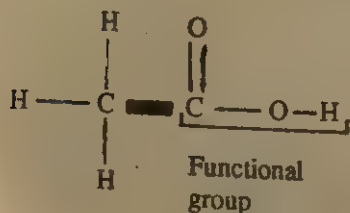
Ethyl alcohol, acetaldehyde and acetic acid are derivatives of the parent hydrocarbon, C_2H_6 , but they contain different functional groups.



Ethyl alcohol



Acetaldehyde



Acetic acid

The study of the properties of these compounds show that these are different from one another.

All compounds with the same functional group will undergo similar reactions. For example, the following alcohols: 1. $\text{CH}_3 - \text{CH}_2 - \text{OH}$, 2. $\text{CH}_3 - \text{CH}_2 - \text{OH}$, and 3. $\text{CH}_3 - \text{CH}(\text{OH}) - \text{CH}_3$, etc.

produce hydrogen on reacting with sodium metal, i.e.,

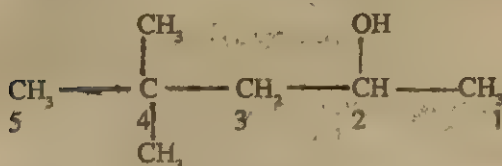


Where $\text{R} = -\text{CH}_3, -\text{CH}_2-\text{CH}_3$ or $\text{CH}_3-\text{CH}=\text{CH}_2$

The similarity in reaction shows that in these reactions only functional group $-\text{OH}$ is involved. The $-\text{C}-\text{C}-$ bonds and $\text{C}-\text{H}$ bonds are quite stable and strong, and thus, do not dissociate easily — whereas $-\text{O}-\text{H}$ is weaker, and hence, more reactive. Most of the organic chemistry is functional group chemistry. Organic chemists have classified organic compounds into categories according to their functional groups. The double and triple bonds of alkenes and alkynes are chemically reactive and are, thus, considered functional groups.

Some typical examples to illustrate the application of IUPAC rules are given below :

Example 7.1 Give the systematic name of the following organic compound :



Solution 1. The functional group present is an alcohol. Hence, the suffix is $-\text{ol}$ (for alcohol the terminal- e of the parent alkane is replaced by $-\text{ol}$)

2. The longest chain containing $-\text{OH}$ functional group has five carbons. Therefore, the parent hydrocarbon is pentane.

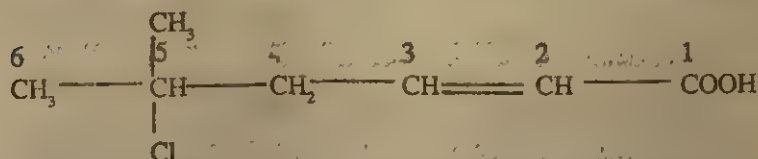
3. The group $-\text{OH}$ is at position 2 (the position of the $-\text{OH}$ group in the carbon skeleton is shown by the lowest number as per IUPAC rules).

4. Two methyl groups are attached to carbon 4.

5. The systematic name is, therefore,

4, 4- Dimethyl - 2 pentanol

Example 7.2 Give the systematic name of the following organic compound.



Solution 1. Here, there are two functional groups, i.e., an alkene and a carboxylic group $-\text{COOH}$. Therefore, suffix should be such which

can indicate both. This could be possible when both the functional groups are combined; i.e., —ene and —oic into —enoic

2. Halogen is treated as a substituent. It is present at carbon 5. In addition to this there is another methyl substituent group at carbon 5.

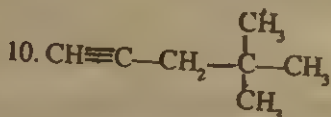
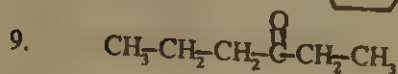
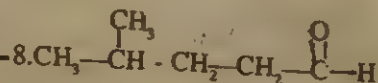
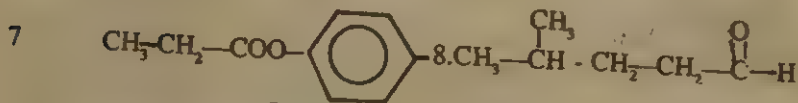
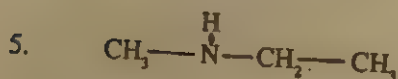
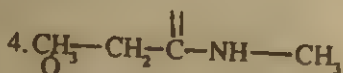
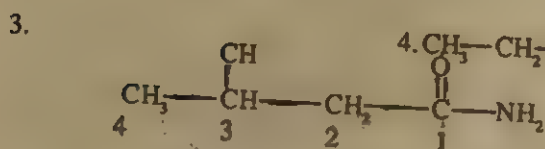
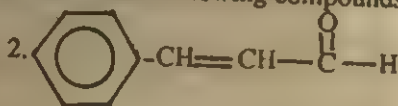
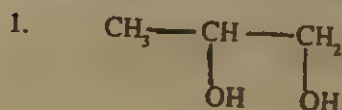
3. The parent hydrocarbon is hexane.

4. The double bond is present between carbon atoms 2 and 3.

5. The systematic name will be :

5-chloro - 5 - methyl - 2 - hexenoic acid.

Example 7.3 : Give the systematic names to the following compounds :



1. The parent hydrocarbon is propane. Two functional groups of the same type are attached at different carbon atoms, 1 and 2. Therefore the name is 1, 2 — Propandiol

2. The parent hydrocarbon is propene. The substituent group C_6H_5 is attached to carbon 3. It contains aldehyde group. The ending 'e' of the hydrocarbon is replaced by —al to designate aldehyde. The functional group should also be given the smallest number when selecting the chain. Hence, the name is 3 - Phenyl - 2-propenal.

3. The parent acid is butanoic acid. The carbonyl carbon should be numbered 1. Amide is named by dropping —ic or —oic ending from the name of the parent acid and adding the ending amide. Hence, the name is 3-Methylbutanamide.

4. The parent acid is propanoic acid and there is a methyl substituent on the amine group. Hence, the name is N - Methylpropanamide.

5. There are two alkyl groups attached to the nitrogen, hence, it is a secondary amine. In naming them, alkyl groups are followed by the word amine. Hence, the name is, Ethyl methyl amine.

6. One alkyl group is attached to the nitrogen, hence, it is a primary amine. Therefore, the name is Propylamine.

7. This is an ester. Esters are named as derivatives of carboxylic acids. This ester is made of propanoic acid and phenol. Hence, the name of the compound is Phenyl propanoate.

8. The parent hydrocarbon is pentane. Hence, the name is 4 — Methylpentanal.

9. The parent hydrocarbon is hexane and the carbonyl group carbon is at position 3. Hence, the name is 3—Hexanone

10. 4, 4 - Dimethyl - 1 - pentyne

Example 7.4 What is the structure of each of the following compounds :

(i) 2, 2, 4, - Trimethylpentane

(ii) 1, 3-Cyclobutadiene

(iii) 3-Methyl - 2- butanone

(iv) 3, 3-Dimethylhexanal

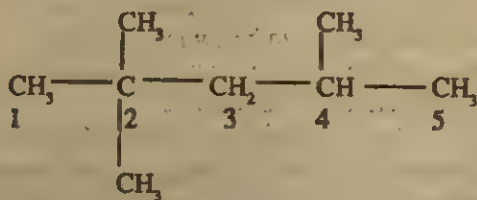
(v) 2-Methylpropanoic acid

(vi) 2-Methyl - 2-propanol

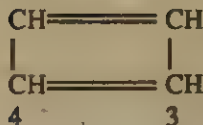
(vii) 1-methyl - 2, 3-diethylbenzene

(viii) 3-Chlorocyclohexene

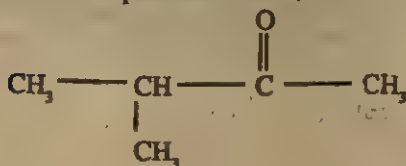
Solution (i). A five atom carbon chain is present and the substituent's are attached to carbon at two places, i.e., two methyl group at position 2 and a third methyl group at position 4. Hence, the structure is,



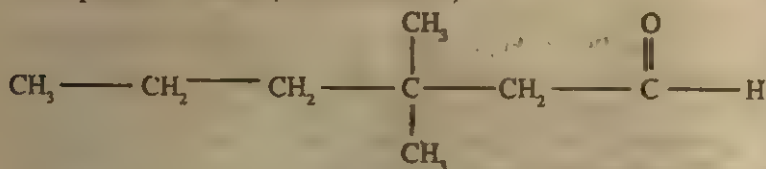
(ii). 1 2 The double bond is present in position 1 and 3, hence, the structure is



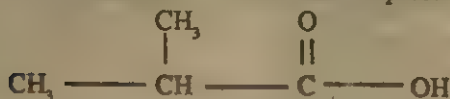
(iii). A four atom carbon chain is present. The carbonyl group is present in 2 position. Hence, the structural formula is,



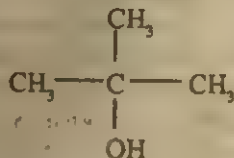
(iv). A six atom carbon chain is present, the aldehyde group is present in position 1. Hence, the structure is,



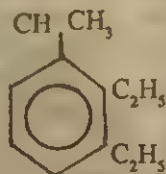
(v). A three atom carbon chain is present. Hence, the structure is,



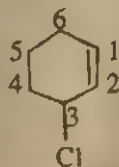
(vi). The carbon chain contains three atoms of carbon. The methyl group and —OH group are attached to the same carbon atom. Hence, the structure is,



(vii). A six membered ring is present as suggested through benzene. The numbering is as shown in the figure. The prefix 1-methyl means that a methyl group is present in position 1. Similarly ethyl groups are present in positions 2 and 3. Hence, the structure is,



(viii). A six membered ring is suggested by cyclohexene. The word 'ene' denotes the presence of a double bond. As per the rules the double bond is to be given the smallest number. The numbering is given below in the figure. The prefix, —3 chloro suggests that this group is attached to carbon 3. Hence, the structural formula is,



7.7 SOME COMMON ORGANIC COMPOUNDS

This section includes some common organic compounds along with their major uses. Compounds containing different functional groups (Table 7.13) have been chosen. Their chemistry will be dealt in later units.

Alkanes : Petroleum is a mixture of different hydrocarbons (solid, liquid as well as gaseous). It has no uses in its raw form. It derives its name from the Latin words 'Petra' (meaning rock) and 'oleum' (meaning oil).

Petroleum (or crude oil) is a black viscous liquid with a characteristic smell. It occurs under the earth's crust entrapped in impervious rocks. It was formed from the decomposition of the remains of marine

animals and plants that were buried in the beds of the seas millions of years ago. These animals and plants had, by the process of photosynthesis, made sugars and other organic compounds that they required to live. During the course of time, high pressures and temperatures and bacterial action converted these compounds into oil. Similar conditions led to the formation of the natural gas that is often found associated with crude oil as well as in deposits on its own. It is mainly methane. It is a good non-poisonous fuel. On refining, it gives various useful products like liquefied petroleum gas (LPG), petrol, kerosene, diesel, furnace oil and wax in the order of increasing carbon contents. The uses of these compounds are listed in Table 7.14. LPG is used as a fuel in houses for cooking purposes.

TABLE 7.14 : Fractions obtained from crude oil and their uses

Fraction	Composition	Boiling point range	Uses
Gas hydrocarbons	C_1-C_3	Below 307 K	As fuel and for making carbon black, hydrogen, gasoline (synthetic petrol by polymerisation)
Petroleum ether	C_3-C_6	303-343K	As solvent and in dry cleaning
Petrol or gasoline	C_6-C_{12}	343-473 K	As motor fuel and for making petrol gas
Kerosene oil	$C_{12}-C_{15}$	473-548 K	Household fuel for heating and lighting and for making oil gas
Gas oil and diesel oil	$C_{15}-C_{18}$	548-623 K	Fuel for diesel engines and furnaces; For cracking also
Lubricating oil, vaseline (petroleum jelly), paraffin wax	C_{18} and higher alkanes	623-673 K	As lubricants and in cosmetic creams; Wax for candle manufacture and water proofing
Pitch and Asphalt	Viscous liquid	Above 673 K	For roofing, surfacing, etc.

The large number of substances which are obtained from petroleum or its fractions are collectively known as petrochemicals. The chief products are shown in Fig. 7.1.

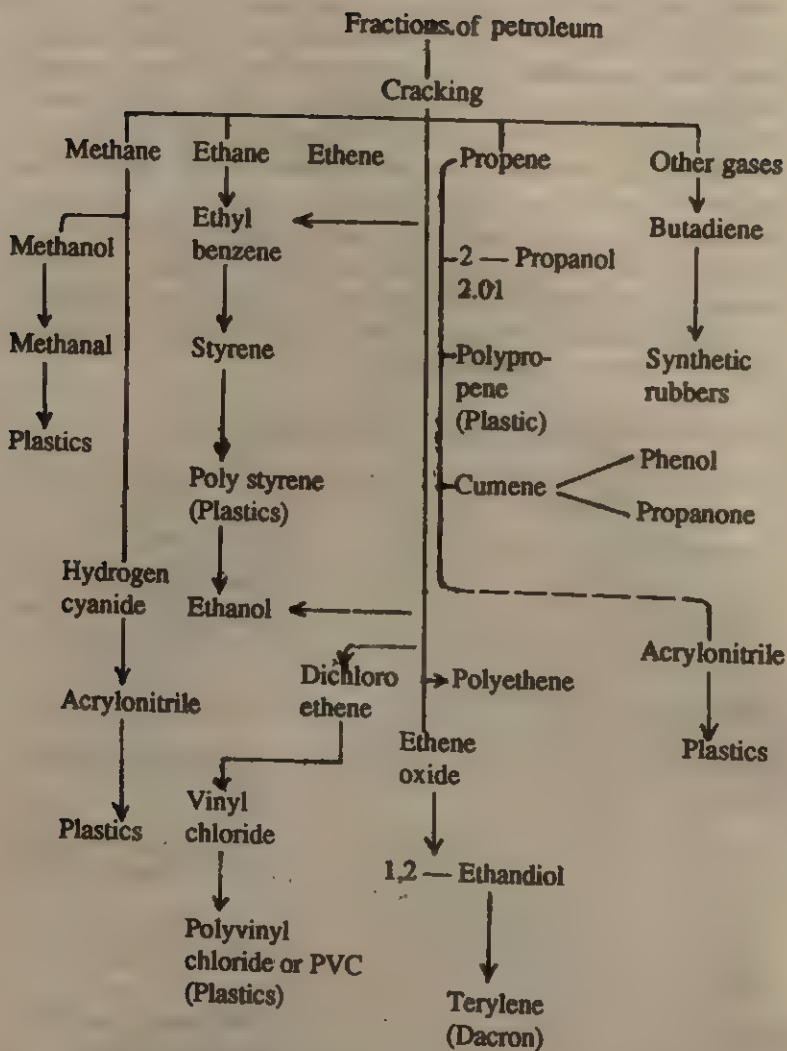


Fig. 7.1 Some chemicals from petroleum

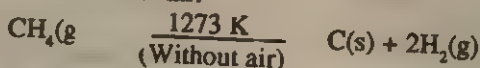
Alkenes : The lower alkenes (C_2 to C_4 or C_5) are obtained as products of petroleum refining which in turn are used to prepare different polymers like polyethene, polypropene, synthetic rubber (from 1, 3 - butadiene) and also other compounds such as alcohols, aldehydes, and ketones on industrial scale (Fig. 7.1).

Alkynes : Acetylene is an important compound of this class which is mainly used for welding purpose.

Uses of Methane, Ethane, Ethylene and acetylene

Methane : It is used,

- (i) As a gaseous fuel. Since it does not burn with sooty flame, its use is quite clean and hygienic.
- (ii) In the industrial preparation of compounds like methyl chloride, chloroform, methyl alcohol, etc.
- (iii) In the preparation of black paints and in rubber industry. Methane decomposes into carbon and hydrogen when heated at 1273K and in the absence of air.



This decomposition reaction is called **pyrolysis**. The carbon formed is used in the preparation of black paints and in rubber industry.

Ethane : It is used,

- (i) As a gaseous fuel
- (ii) In the industrial preparation of organic compounds like ethyl alcohol, nitroethane, etc.

Ethylene : It is used,

- (i) In the manufacture of polyethene, a plastic material used for making toys, bags, pipes, boxes, etc.
- (ii) As a general anaesthetic
- (iii) In the preparation of a large number of organic compounds, *e.g.*, glycol, ethyl halides, ethyl alcohol, etc.
- (iv) For ripening of fruits by exposing them to ethylene atmosphere.
- (v) As a substitute for acetylene in oxyacetylene flame.

Acetylene : It is used,

- (i) For producing oxyacetylene flame used in cutting and welding purposes.
- (ii) For the manufacture of a large number of organic compounds, *e.g.*, acetaldehyde, acetone, acetic acid, alcohol, western (tetra-chloroethane), etc.
- (iii) For ripening of fruits
- (iv) For illumination in hawker's lamps.

Arenes : Arenes are a class of carbon compounds also called aromatic compounds because many have pleasant odours. Petroleum and coal are the sources of most hydrocarbon molecules. The hydrocarbons in crude oil are mostly alkanes and cycloalkanes whereas those in coal are mostly aromatic benzene, naphthalene, anthracene and a host of others (Fig. 7.2). Benzene, toluene and xylene are used to manufacture synthetic detergents, synthetic fibers and explosives (*e.g.* TNT).

Many artificial dyes used in textile industry are obtained from naphthalene and anthracene. Mothballs made of naphthalene are used to protect woollens from insects.

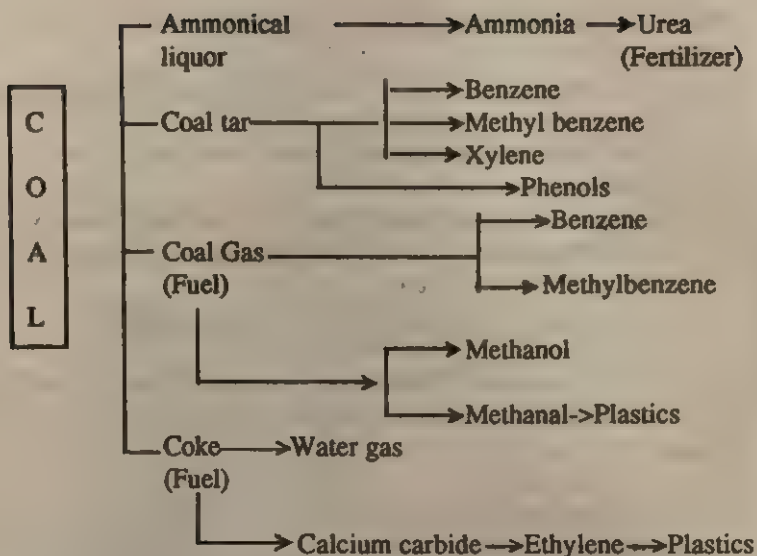


Fig. 7.2 Chief organic chemicals produced from coal.

Alcohols : Many aliphatic alcohols are used in the laboratory, clinic and industry. Isopropyl alcohol, a colourless liquid, is used for massages and to lower the body temperature in fever. It is also used as a base for perfumes, creams, lotions and other cosmetics. Ethyl alcohol and methyl alcohol are the two most important alcohols. Ethanol is mainly obtained from ethene and is manufactured by fermentation of molasses (sugar) and starch. Methyl alcohol is mainly obtained from petroleum feedstock. Both the alcohols are of industrial importance.

Ethyl alcohol is used,

1. As alcoholic beverage
2. In the manufacture of drugs, dyes, paints, synthetic rubber, varnishes, lacquers, etc.
3. As a petrol substitute (power alcohol)
4. In the preparation of a large number of organic compounds like aldehydes, carboxylic acids, iodoform, etc.
5. As a fuel in spirit lamps and stoves
6. As a preservative for biological specimens
7. As a solvent for pharmaceutical preparations
8. As a fuel from a renewable source like sugarcane

Note. Alcohol for industrial purposes is denatured by the addition of substances, e.g., methyl alcohol, pyridine, copper sulphate, etc. that make it unfit for drinking.

Compounds derived from 2-ethylhexanol are used as softners in plastic industry. Ethylene alycol is used in antifreezes. It is used in the manufacture of dacron (Fig. 7.1).

Glycerol (1, 2, 3-propantriol) is used as a lubricant in suppositories and as a moistening agents in cosmetics, tools and drugs. Glycerol is also an important ingredient of fats and oils.

Harmful Effects of Drinking Alcohol, i.e. Ethylalcohol

Alcoholic beverages are prepared from different starting materials like molasses, barley, grapes, etc., by alcoholic fermentation. These contain large amounts of water, colouring and flavouring materials besides ethyl alcohol. These beverages are consumed throughout the world because when taken internally it stimulates the human system. Ethyl alcohol, if taken in small quantity, is harmless but its continuous use results in addiction. Addiction to alcohol induces many bad habits. Under its influence a person fails to distinguish between good and bad, or right and wrong. He speaks and behaves very abnormally. Alcoholism contributes to family conflicts, divorces, automobile accidents, vandalism, violent crimes, etc. This habit leads to total economic disaster of a family. Constant use of alcohol ruins health and may even cause death. Despite its bad effects drinking of alcohol is considered a very important social status symbol.

Methanol is toxic in nature. Its small amount when taken internally causes even poisoning coupled with blindness. Consumption in large quantities can be fatal. So it is not a drinking alcohol.

Aldehydes and Ketones : A large number of aldehydes and ketones have been isolated from plants and animals. Compounds with high formula weights have fragrant or penetrating odours. Methanal (formaldehyde or formalin) and ethanal (acetaldehyde) are two important aldehydes. Methanal is manufactured by the oxidation of methyl alcohol.

Uses of Formaldehyde

- (i) It is used as an antiseptic and disinfectant
- (ii) A 40% aqueous solution of formaldehyde (formalin) is used for preservation of biological and anatomical specimens.
- (iii) With ammonia it forms urotropine which is used as a urinary antiseptic.
- (iv) It is used in the preparation of synthetic plastics like Delrin, Bakelite and Galalith.
- (v) It is used in silvering mirror.
- (vi) It is used in the manufacture of synthetic dyestuffs such as para rosaniline, indigo, etc.
- (vii) It is used for the manufacture of sole leather and water proof fabrics.
- (viii) It is used in the manufacture of hexamine which on nitration produces a powerful explosive (cyclonite or R D X)

Ethanal is manufactured by the oxidation of ethenol. Mainly it is employed in the manufacture of ethonic acid and a limited range of plastics

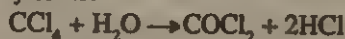
Propanone is manufactured by the dehydrogenation of 2-propanol. It is widely used as a solvent and as an intermediate in the manufacture of other organic compounds, such as ethanoic anhydride, trichloromethane, etc. 2-Butanone is an important laboratory and industrial solvent.

Cyclohexanone is an intermediate in the manufacture of nylon. Benzaldehyde is the simplest aromatic aldehyde. It has pleasant almond odour. Vanillin is responsible for imparting popular vanilla flavour.

Acetone is an industrially important solvent. It is used as a solvent for resins, plastics and varnishes and is often found in nail polish removers.

Halides : Chlorinated compounds of methane ethane and ethene find their use as solvents, e.g., dichloromethane, trichloromethane (chloroform) tetrachloromethane (carbon tetrachloride), 1, 2 dichloroethane, trichloroethene and tetrachloroethene. Tribromomethane CHBr_3 (bromoform) is used in froth flotation methods for mineral purification. Iodoform (CHI_3) is used as an antiseptic. 1, 2-Dibromoethane is mainly used as a fumigant against insects in food storage godowns. 1-Bromo -1-chloro -2, 2, 2-trifluoroethane is used as anaesthetic.

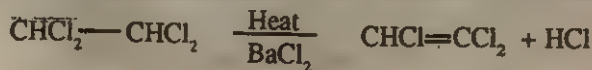
Some important halogen compounds (e.g., solvents, insecticides, etc.) : Carbon tetrachloride, CCl_4 , because its vapours are non-inflammable, is an important industrial solvent and is also used as a fire extinguisher under the name of 'pyrene'. At high temperatures, in presence of water vapours, it forms carbonyl chloride which is extremely toxic.



Hence, after use of pyrene fire extinguisher, the rooms should be thoroughly ventilated. It is used in the production of fluorinated hydrocarbons.

Westron or acetylene tetrachloride, $\text{CHCl}_2\text{---CHCl}_2$, is a heavy non-inflammable but very toxic liquid, b.p. 419K. It is commercially used as a solvent for rubber, oils, fats, paints, varnishes, etc.

Westrosol which is a much less toxic solvent than Westron can be obtained from it as follows :

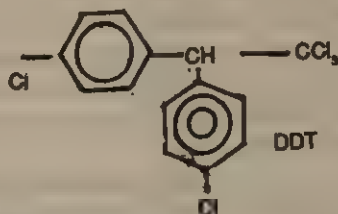


It is used for the dry cleaning of clothes.

Freon 12, dichlorodifluoromethane, CCl_2F_2 is a non-toxic, and non-inflammable liquid commonly used as a refrigerant. It is the most common spray-can propellant. Though it is itself non-toxic, it has been indirectly linked as a cause for skin-cancer. There had been a controversy in the 1970's concerning the partial destruction of the ozone layer in the atmosphere by spray-can propellants and other agents*. Our main protection from the harmful ultraviolet light from the sun is the ozone layer in the atmosphere. If the concentration of the ozone is diminished, toxic effects like increase in the incidence of skin-cancer, are likely to occur.

DDT, 2,2-bis-(p-(chlorophenyl))-1,1,1-trichloroethane, has been an important commercial insecticide. Its use has been banned in some western countries.

The trade name DDT is based on its earlier name (which is incorrect) dichlorodiphenyl trichloroethane.



BHC, benzene hexachloride, $\text{C}_6\text{H}_6\text{Cl}_6$ also known as gammexane, lindane or 666, exists as a number of stereoisomers. The γ -isomer is a powerful insecticide.

There are many other chloroinsecticides. A word of caution . Insecticides are poisonous to human beings and animals and also often accumulate in our bodies causing irreparable damage. Further the insects develop immunity to these, so that more quantities and more powerful (often more harmful to human and animals) insecticides have to be used. Therefore, the move is for 'Organic farming'.

Acids : The simple carboxylic acids like methanoic acid (formic acid) and ethanoic acid (acetic acid) are present in ants and vinegar respectively.

Acetic acid is used :

1. As a coagulant in the manufacture of rubber from latex
2. In the manufacture of various dyestuffs, perfumes and rayon, plastics and paints.
3. For manufacturing pickles
4. For making photographic films
5. In the form of (i) lead tetra-acetate as good oxidizing agent, (ii) white lead and basic copper acetate as paints.
6. For making cellulose ethanote an important synthetic fibre

*The fluorocarbon (e.g. CF_2Cl_2) in the spray cans are decomposed by U.V. light (from the sun) to chlorine atoms (free radicals) which catalyze decomposition of ozone oxygen. Oxides of nitrogen (free radicals) introduced into the upper atmosphere by nuclear explosions, fertilizers and supersonic transport exhaust also decompose ozone to oxygen.

7. For making transparent wrapping materials
8. In pharmaceuticals and in the food industry. Sodium and potassium salts of dodecanoic (C_{12}), hexadecanoic (C_{16}) and octadecanoic (C_{18}) acids are used as soaps. Vegetable cooking oils and vanaspati are also produced from these chain acids.

Nitro Compounds : Nitroalkanes, *e.g.*, nitromethane and nitroethane are useful as solvents. Nitrobenzene is another useful industrial solvent. Aromatic nitrocompounds are used as explosives, *e.g.*, T.N.T. and nitro-cellulose are also used as explosives.

Amines : Aliphatic amines are used in the manufacture of a wide variety of products like drugs, fibers, dyes and insecticides. Aniline, the most important aromatic amine, is used in the manufacture of dyes (via the diazonium salts). Antioxidants and vulcanisation accelerators for the rubber industry. It is also used in sulphadiazine drugs. The diazonium salts, obtainable from primary aromatic amines, can be converted to a variety of products.

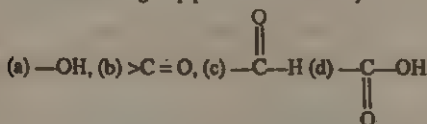
Amino acids which contain two functional groups, the amino group — NH_2 and the carboxyl group — $COOH$ are the constituent of proteins which are the building blocks of living things.

SELF ASSESSMENT QUESTIONS

MULTIPLE CHOICE QUESTIONS

7.1 Put a tick (✓) against the suitable choice :

- (i) A saturated hydrocarbon contains
 - (a) double bond, (b) single bonds, (c) a triple bond connecting individual carbon atoms.
- (ii) Compounds having the same molecular formula but different structural formulae are known as
 - (a) isomers, (b) isotopes, (c) allotropes (d) none
- (iii) The compound with structural formula $CH_3-CH=CH_2$ is known as,
 - (a) propyne, (b) propane, (c) propene, (d) propylene
- (iv) The general formula for alkenes is
 - (a) C_nH_{2n} , (b) C_nH_{2n-2} , (c) C_nH_{2n+2} , (d) C_nH_{2n+1}
- (v) The functional group present in an aldehyde is



- (vi) The molecular formula, C_3H_8O represents
 - (a) an aldehyde, (b) a ketone, (c) an alcohol, (d) an acid
- (vii) In a homologous series, each member differs from its adjacent neighbour by a unit
 - (a) $-CH_3$, (b) $-CH_2-$, (c) $-CH_2-CH_2-$, (d) $-CHO$
- (viii) Which one of the followings is used for ripening of green fruits ?
 - (a) methane, (b) ethane, (c) ethylene (d) acetylene.
- (ix) Acetone and methyl alcohol are obtained from :
 - (a) plant sources, (b) animal sources, (c) water (d) none

- (x) C_2H_4 and C_3H_4 are the first two members of the homologous series of
(a) alkanes, (b) alkenes, (c) alkynes (d) alkanol
- (xi) The IUPAC name for CH_3CHO is
(a) acetaldehyde, (b) formaldehyde, (c) methylaldehyde, (d) ethanal
- (xii) The IUPAC name of the compound having the formula, $H_2C=C(CH_3)-CH=CH_2$ is (IIT 1984).
(a) 3, 3, 3-trimethyl - 1 - propene (b) 1,1,1-trimethyl - 2 - propene
(c) 33, -dimethyl - 1- butene (d) 2, 2-dimethyl - 3-butene (IIT 1986)
- (xiii) An isomer of ethanol is
(a) methanol (b) diethyl ether (c) acetone (d) dimethyl ether (IIT 1986)
- (xiv) The highest boiling point is expected for
(a) iso-octane (b) n-octane (c) 2,2,3,3-tetramethyl butane (d) n-butane (IIT 1986)
- (xv) Only two isomeric monochloro derivatives are possible for
(a) n-butane (b) 2,4-dimethylpentane (c) benzene (d) 2-methylpropane (IIT 1986)
- (xvi) CO_2 is isostructural with (a) $HgCl_2$ (b) $SnCl_2$ (c) C_2H_2 (d) NO_2 (IIT 1987)
- (xvii) The IUPAC name of the compound $CH_2=CH-CH(CH_3)_2$ is (IIT 1987)
(a) 1, 1-dimethyl -2-propene (b) 3-methyl -1-butene (c) 2-vinyl propane (d) 1-isopropyl ethylene

7.2 Match the terms in Column 'A' with the terms/descriptions in column 'B'.

Column A		Column B
1. Organic chemistry	(a)	Carbon-carbon double bond
2. Hydrocarbon	(b)	Contains $-COOH$ group
3. Alkane	(c)	Carbon-carbon triple bond
4. Alkyl group	(d)	C_nH_{2n+2}
5. Isomers	(e)	Contains $-OH$ group
6. Alkene	(f)	Chemistry of carbon
7. Alkyne	(g)	C and H only
8. Alcohol	(h)	Same molecular formula with different structural formulae
9. Aldehyde	(i)	Contains $-CHO$ group
10. Carboxylic acid	(j)	Contains one hydrogen atom less than parent alkane

7.3 Fill in the blanks in the following:

- The organic compounds having $-CHO$ functional group are known as ____.
- The next higher homologue of ethane is ____.
- The IUPAC name of methyl alcohol is ____.
- The general formula of ____ is C_nH_{2n+2} .
- The two allotropic forms of carbon are ____ and ____.
- An atom or a group of atoms which gives the organic molecules its characteristic chemical properties is called a ____.
- The ____ properties of compounds containing same functional group are similar.
- The IUPAC name of ____ is ethanoic acid.
- An acid is represented by the functional group ____.
- The alcohol used for driving purposes is called ____.
- The structural formula for propane is ____.
- A 40% aqueous solution of formaldehyde is known as ____.
- Acetic acid forms an ice like crystal, therefore, this acid is known as ____.
- The ability of carbon atom to unite with other carbon atoms is known as ____.
- The valency of carbon in ethylene is ____.
- Compounds of carbon and hydrogen are called ____.
- Butane is a ____.
- Acetylene is an ____.

- (19) Oxyacetylene flame is used in———.
- (20) The process of burning of a hydrocarbon in the presence of excess of air to give CO_2 , H_2O , light and heat is known as———.

7.4 Choose the correct statements of the followings :

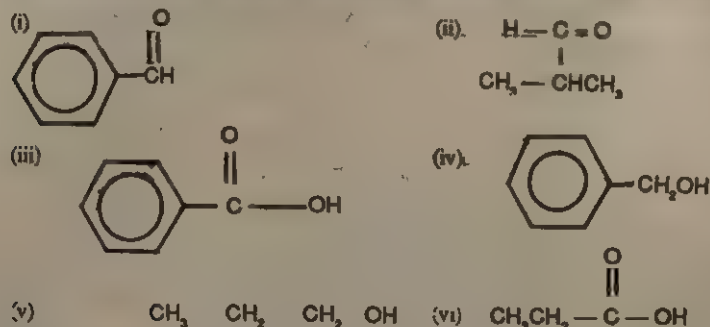
- (1) The compound whose formula is C_3H_6 must be an alkene.
- (2) Molecules with carbon to carbon multiple bonds readily undergo addition reactions.
- (3) Chemical bonds formed between carbon and carbon or hydrogen in organic compounds are generally covalent in nature.
- (4) The IUPAC name for $\text{C}_3\text{H}_7\text{CHO}$ is propanol.
- (5) The IUPAC name for CH_3COCH_3 is propanol.
- (6) Two consecutive members of the same homologous series differ from each other by $-\text{CH}_2-$ unit.
- (7) Acetylene is used in the ripening of green fruits.
- (8) An alkyl group describes an organic group formed when two atoms of hydrogen are taken from an alkane.
- (9) Alkenes and alkynes are unsaturated hydrocarbons.
- (10) Aldehydes contain hydrogen atom bonded to the carbon present in a carbonyl group.

SHORT ANSWER QUESTIONS

7.5 (a) Classify the following compounds as alkanes, alkenes, or alkynes :

- (i) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ (ii) C_6H_{16} (iii) $\text{CH}\equiv\text{CH}$
 (iv) $\text{CH}_3\text{CH}=\text{CHCH}_3$ (v) $\text{CH}_3(\text{CH}_2)_6\text{CH}_3$
 (vi) $\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}\equiv\text{CH}$ (vii) $-\text{CH}_2-\text{CH}(\text{CH}_3)_2$
 (viii) C_6H_6 (ix) $\text{CH}_2=\text{CH}_2$ (x) CH_3-CH_3

(b) Classify the following compounds according to the kind of functional group present:



- (c) In how many different ways can you arrange the atoms in the compound having the formula C_5H_{12} ? What term is used to describe each different compound having the same molecular formula?
- (d) Draw the structures of four alcohols that have the formula $\text{C}_4\text{H}_{10}\text{O}$.
- (e) What is the difference in the molecular formula of any two adjacent members of a homologous series of hydrocarbons, (i) in terms of molecular mass, and (ii) in terms of number and kind of atoms in their molecular formulae.
- (f) Select the hydrocarbons from the followings which are members of the same homologous series. Also give the name of each homologous series representing the hydrocarbons.
 CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_4H_{10} , C_3H_4 , C_3H_6

- (g) (a) For each of the following molecular formulae, indicate whether the compound should be an alcohol, an aldehyde, a ketone, or an acid :
 (i) CH_4O (ii) $\text{C}_2\text{H}_6\text{O}$ (iii) $\text{C}_2\text{H}_4\text{O}_2$ (iv) $\text{C}_3\text{H}_6\text{O}$ (v) CH_2O
- (h) Name the element present in all the following substances : wood, carbohydrates, graphite, petrol, paper, diamond, vitamins, plastics.
- (i) Name the allotropic form of carbon having the following properties :
 (a) It is a good conductor of electricity, and (b) It is soft .
- (j) What is the common parent hydrocarbons of the following organic compounds ?
 (i) ethyl alcohol, (ii) acetaldehyde, and (iii) acetic acid.
- 7.6 (a) Name two organic compounds which are obtained from plant sources, and two which are obtained from animal sources.
- (b) Define the terms (i) organic chemistry, and (ii) organic compound.
- (c) What is meant by a functional group ? Name three compounds representing different functional groups.
- (d) What functional groups are present in
 (i) CH_3CHO (ii) $\text{CH}_3\text{CH}_2\text{OH}$ (iii) $\text{CH}_3\text{CH}_2\text{COOH}$?
- 7.7 (i) Write structural formulae for all the isomeric alcohols having the molecular formula. $\text{C}_4\text{H}_{10}\text{O}$ (IIT 1984)
- (2) Write the structure of all the possible isomers of dichloroethene. Which of them will have zero dipole moment ?
- (3) Write the IUPAC name of, $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCOOH}$ (IIT 1986)
- (4) Graphite is a better lubricant on the moon than on the earth. Comment. (IIT 1986)
- (5) What happens when CO_2 is passed through a concentrated aqueous solution of sodium chloride saturated with ammonia. (IIT 1988).

TERMINAL QUESTIONS

- 7.1 What is organic chemistry ?
- 7.2 Why do so many different organic compounds exist ?
- 7.3 Why do carbon atoms form four bonds ?
- 7.4 What is allotropy ? Name various allotropic forms of carbon.
- 7.5 Write a brief description on the followings :
 (a) tetravalency of carbon (b) carbon chain
 (c) carbon-carbon double bond (d) carbon-carbon triple bond
- 7.6 (a) What are hydrocarbons? (b) What is an alkane ? (c) Why are alkanes said to be saturated ?
- 7.7 (a) What are structural isomers ?
 (b) Suggest as many different isomers as you can that have the formula C_5H_{12} .
- 7.8 (a) How does each of the followings differ from an alkane.
 (i) alkene, and (ii) alkyne ? Why are alkenes and alkynes considered unsaturated ?
- 7.9 What is a functional group ?
 List a few functional groups that you have come across in this unit.
- 7.10 What is fermentation? How is alcohol obtained by fermentation process ? What is an alcohol ?
- 7.11 (a) What do you understand by homologous series ? Explain giving one example of a homologous series.
 (b) What are the characteristic features of homologous series ?
- 7.12 Explain the differences in the properties of diamond and graphite based upon their structures.
- 7.13 Give equations for the following :
 (a) Preparation of carbondioxide
 (b) Basic properties of sodium carbonate solutions.
 (c) Formation of acetylene

- 7.14 What are carbides ? Describe a few types of carbides.
 7.15 What is the basic difference between inorganic chemistry and organic chemistry ?
 7.16 Write a short note on fluorocarbons.
 7.17 How does water gas differ from producer gas ?
 7.18 List the important uses of alcohols, halides and nitrocompounds.

ANSWERS TO SELF ASSESSMENT QUESTIONS

- 7.1 (i) (b). (ii) (a). (iii) (c). (iv) (a). (v) (c) (vi) (c). (vii) (b). (viii) (d). (ix) (a). (x) (b). (xi) (d). (xii) (c). (xiii) (d). (xiv) (b). (xv) (a) and (d). (xvi) (a) and (c) (xvii) (b).
 7.2 (1) (f). 2. (g). 3. (d) 4. (j) 5. (h) 6. (a) 7. (c) 8. (e) 9. (i) 10. (b)
 7.3 1. Aldehydes 2. Propane 3. Methanol 4. Alkanes 5. Diamond, graphite
 6. Functional group 7. Chemical 8. Acetic acid 9. —COOH
 10. Alcoholic beverage 11. $\text{CH}_3\text{CH}=\text{CH}_2$ 12. Formalin
 13. Glacial acetic acid 14. Catenation 15. Four 16. Hydrocarbons
 17. Saturated hydrocarbon 18. Unsaturated hydrocarbon 19. Welding metals
 20. Combustion

7.4 Statement 1, 2, 3, 6, 7, 9 and 10 are correct.

- 7.5 (a) Alkanes : (ii), (v) (vii), (x)
 Alkenes : (i), (iv), (viii), (ix)
 Alkynes : (iii), (vi)

- (b) Alcohols : (iv), (v)
 Aldehydes : (i), (ii)
 Carboxylic acids : (iii), (vi)

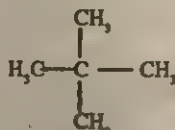
- (c) (i) $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$ (iii)

Pentane

- (ii) $\text{CH}_3\text{—CH—CH}_2\text{—CH}_3$



2-Methyl butane



2, 2-Dimethylpropane

Isomers

- (d) (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
 1-Butanol

- (ii) $\text{CH}_3\text{CH}_2\text{CH—CH}_3$



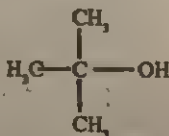
2-Butanol

- (iii) $\text{CH}_3\text{—CHCH}_2\text{OH}$



2-Methylpropanol

(iv)



1, 1 — Dimethyl ethanol

- (e) (i) 14 (ii) $\text{—CH}_2\text{—}$

- (f) Homologous series :

Alkane CH_4 , C_2H_6 , C_4H_{10}

Alkyne C_2H_2 , C_4H_6

Alkyne C_2H_2 , C_4H_6

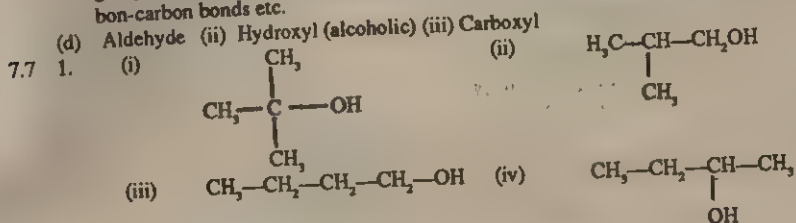
- (g) (i) Alcohol, (ii) Alcohol, (iii) Acid (iv) Aldehyde or ketone (v) Aldehyde

- (h) Carbon

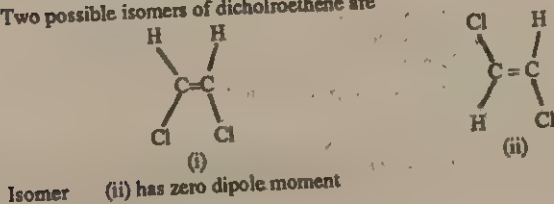
- (i) Graphite

- (j) Ethane

- 7.6 (a) Plant sources : Sugar, Cellulose; Animal Sources : Urea, Hormones
- (b) (i) Organic chemistry is the study of substances that contain carbon-hydrogen bonds.
- (ii) Organic compounds are compounds of carbon characterized by their non-ionic nature, inflammability, etc.
- Compounds like CO , CO_2 , etc. are not organic compounds. Also compounds formed of only carbon and nitrogen are not included among organic compounds.
- (c) The functional group is an atom or a group of atoms which gives an organic compound its reactivity. It is joined to an alkyl group which forms the homologous series. It gives the chemical characteristics of a compound. A long carbon chain with many carbon atoms reduces the chemical activity of the functional group. Examples of functional groups are hydroxyl, carbonyl, unsaturated carbon-carbon bonds etc.



2. Two possible isomers of dichloroethene are



3. 2-Pentenoic acid
4. It is due to lack of gravity on moon.
5.
$$\text{NaCl} + \text{NH}_4\text{OH} + \text{CO}_2 \longrightarrow \text{NaHCO}_3 + \text{NH}_4\text{Cl}$$

Energetics

Although a typical chemical reaction may appear far removed from the working of an engine, the same fundamental principles of heat and work apply, to both.

F.T. WALL

UNIT PREVIEW

- 8.1. Introduction
 - 8.2. Units
 - 8.3. Some commonly used terms
 - 8.4. Internal energy
 - 8.5. Enthalpy and enthalpy changes
 - 8.5.1. Meaning of enthalpy
 - 8.5.2. Enthalpy change
 - 8.5.3. Standard states, symbols and conventions
 - 8.5.4. Conservation of energy in a chemical reaction
 - 8.5.5. Origin of enthalpy change in a reaction
 - 8.6. Hess' law of constant heat summation
 - 8.7. Heats of reactions
 - 8.7.1. Heat of neutralization
 - 8.7.2. Heat of combustion
 - 8.7.3. Heat of formation
 - 8.7.4. Heat of fusion and vapourization
 - 8.8. Sources of energy
 - 8.9. Criteria for spontaneous change
 - 8.10. Why the energy crisis if energy is conserved in Nature ?
- Self assessment questions
Terminal questions
Answers to self assessment questions

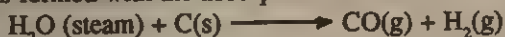
LEARNING OBJECTIVES

- At the completion of this unit, you should be able to :
1. Understand adiabatic and isothermal conditions.
 2. Distinguish between exothermic and endothermic changes.
 3. Differentiate between the energy forms, heat and work.
 4. Understand internal energy of a system.
 5. Define enthalpy, (H) and change in enthalpy, (ΔH).
 6. Recognise that for a constant volume reaction, $q_v = \Delta E$.
 7. Recognise that for a constant pressure reaction, $q_p = \Delta H$.
 8. Know that state functions such as E , H , V , P , and T are independent of their history.
 9. Interpret the sign conventions used in writing a thermochemical equation.
 10. Apply Hess' law to calculate ΔH of a reaction when given enthalpy changes for other reactions.
 11. Define various heat of reactions, i.e., heat of formation, neutralization, combustion, formation, fusion and vapourization.
 12. Calculate heat of reactions.
 13. Calculate ΔH for a reaction when given the values of bond energies.
 14. Know various sources of energy.
 15. Distinguish between spontaneous and non-spontaneous changes.
 16. Recognise that entropy is a measure of the disorder of a system.

17. Predict the sign of ΔS for physical and chemical processes.
18. Use the relation $\Delta G = \Delta H - T \Delta S$ to calculate ΔH , ΔS and T when given any two of the three quantities for the system.

8.1 INTRODUCTION

The idea that chemical reactions can produce heat should not be new to you. You may recall many chemical reactions which produce heat *e.g.*, burning of coal, combustion of food in the body, sodium reacting with water *etc.* On the other hand, there are large number of reactions which absorb heat *e.g.*, when steam is passed over red hot coke, water gas is formed with the absorption of heat.



When a chemical reaction occurs, bonds of reacting molecules are broken with the absorption of heat, at the same time new bonds are formed which evolve heat. We can say that, "the energy changes in a chemical reaction are the result of bond breaking and bond forming events".

Heat is not the only energy which is involved in a chemical reaction. Energy can be released or absorbed in other forms as well. When acidulated water is electrolysed, it is the electrical energy which is being absorbed. In the photochemical reactions, energy in the form of light is being absorbed, *e.g.*, photosynthesis in the plants. In this unit we shall study the heat energy changes involved in chemical reactions.

8.2 UNITS

All forms of energy can be measured in joules, abbreviated as J. However, calorie or kilocalories (kcal) was quite popular as a unit to measure heat before adoptions of SI units. It is still being used in some countries. The relationships between joule and other units of energy are given below :

$$\begin{aligned} 1\text{J} &= 1 \text{ kg m}^2 \text{ s}^{-2} \\ &= 10^7 \text{ ergs} \\ &= 0.2390 \text{ cal} \\ &= 2.390 \times 10^{-4} \text{ kcal} \\ &= 1 \text{ Nm} \end{aligned}$$

Exercise 8.1 : What will be the final temperature of 1 kg of material at 300 K after 15.0 kcal of heat is transferred from it ? The specific heat of the material is 1.2 cal/deg - g.

Solution : Loss in temperature = $\frac{15.0 \times 1000}{1.20 \times 1.0 \times 1000} = 12.5\text{K}$

$$\text{Final temperature} = 300 - 12.5 = 287.5 \text{ K or } 14.5^\circ\text{C}.$$

8.3 SOME COMMONLY USED TERMS

In the study of chemical energetics, the following terms are frequently used.

System : It is any part of the universe which is selected for investigations.

Surroundings : The whole of the universe which is around the system is known as surroundings. A system may exchange matter and energy from the surroundings. For example, consider a reaction taking place in a conical flask, here the conical flask and everything else around the reaction mixture are considered the surroundings.

A system, in general, can be of three types :

- (i) **Open System :** A system which can exchange both matter as well as energy with its surroundings is called an open system. Consider evaporation of water kept in a beaker. Here water takes heat from the surroundings and evaporates. Water vapour can also condense into it. Thus it is an open system.

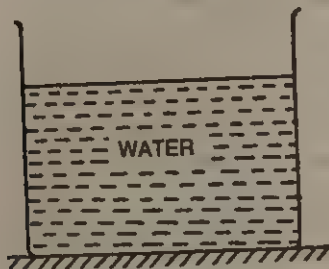


Fig.8.1. An open system.

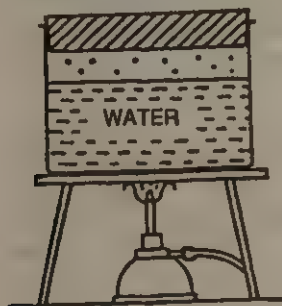


Fig.8.2. A closed system

- (ii) **Closed System :** A system which can exchange energy but not matter with its surroundings is called a closed system. For example, warming water in a closed vessel (Fig. 8.2). Here heat energy can enter and escape from the system but not water vapours. Matter can neither be added to nor removed from it.

(iii) **Isolated System :** A system which can exchange neither energy nor matter with its surroundings is called an isolated system. Water kept in a perfectly insulated thermosflask. As flask is insulated, exchange of energy and matter with the surroundings is not possible.

Adiabatic Change : If a change takes place in such a way that there is no exchange of heat between the system and its surroundings, the change is said to be adiabatic. Adiabatic conditions can be achieved by insulating the interface or boundary between the system and its surroundings. An example is a reaction carried out in a thermosflask.

Isothermal Change : The chemical or physical changes, where the system and surroundings are in thermal contact and heat is exchanged between the two in such a way that the temperature remains constant, are known as isothermal changes.

State of a System : While investigating a system, it is necessary to know its properties before and after a change. This can be done by specifying the temperature, pressure, number of moles of each component and their physical forms. When these variables are specified, the state of the system is known precisely.

State Functions : Properties of a system such as temperature, pressure, internal energy, enthalpy which depend only on the state of the system, no matter how that state is attained, are known as state functions.

Direction of Heat Flow : Consider the arrangement of two beakers A and B filled with water (Fig. 8.3). Though A has lesser quantity of water, yet on opening the stopper, S, water flows from the

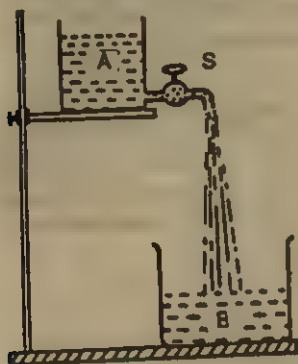


Fig. 8.3. Flow of water from higher level to lower level

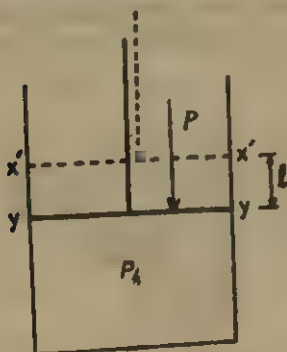


Fig. 8.4. Pressure volume work.

beaker A to beaker B. Water will never flow from beaker B to beaker A of its own, i.e., without the external help. Why? The answer to this question is, "the beaker A is at the higher level than the beaker B, and as such water in it has higher potential energy". Similarly when a system and its surroundings differ in (i) temperature or (ii) pressure, exchange of energy between the two can take place. As water flows from higher level to lower level, similarly, heat flows from higher temperature to lower temperature until the two i.e., system and its surroundings attain the same temperature. Temperature does not measure the quantity of heat energy, it simply predicts the direc-

tion to which heat energy can flow. When there is a difference in pressure, energy flows in the form of work. Consider a system con-

sisting of a cylinder 'C' fitted with a frictionless and weightless piston. When the piston has position as shown by yy (Fig.8.4) pressure inside the cylinder and atmospheric pressure are P_1 and P respectively. Let P_1 be greater than P , then the piston will move upward till the pressure inside the cylinder is also P atm, the new position of the piston is xx and the change in the volume of the gas inside the cylinder is ΔV . In this process the system does work equivalent to $P \cdot \Delta V$ on the surroundings and an equivalent amount of energy in the form of work is transferred to the surroundings by the system.

Sign Conventions : The sign convention that applies is that when a system absorbs heat, say ' q ', it is a positive quantity. q is negative when the system loses heat.

w is a positive quantity when work is done by a system. w is a negative quantity when work is done on the system.

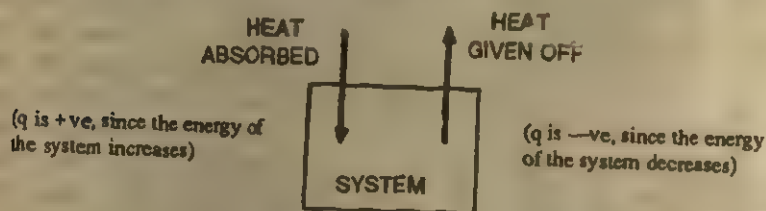


Fig. 8.5. Sign convention for heat flow

8.4 INTERNAL ENERGY

The internal energy, E of a substance is the sum of all the types of energies a substance can possess. This includes energies due to translational, rotational and vibrational motions (Fig. 8.6), coulombic energies between electrons and nuclei in atoms and the potential energies due to attractive or repulsive forces acting between molecules.

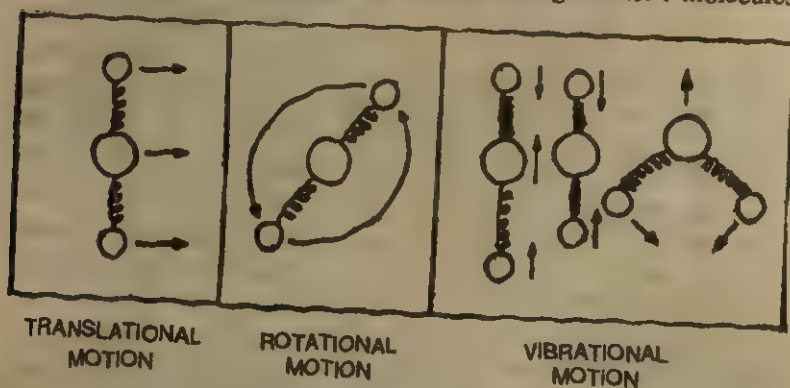


Fig. 8.6. Three kinds of motions that a molecule may possess, each contributes to the total kinetic energy.

The absolute value of internal energy cannot be determined. However, the change in internal energy, ΔE , can be experimentally measured from the change in the properties of the system.

$$\Delta E = \Sigma E(\text{products}) - \Sigma E(\text{reactants}) \quad (8.1)$$

When a closed system absorbs heat, q some of the energy is consumed in increasing the internal energy, ΔE , of the system and the rest is used up in doing pressure-volume work, $P \Delta V$. Therefore,

$$q = \Delta E + P \Delta V \quad (8.2)$$

If the volume remains constant,

$$\Delta V = 0$$

$$\text{or } q_v = \Delta E \quad (8.3)$$

i.e., the total heat supplied to the system at a constant volume is used up in increasing the internal energy of the system.

When heat is absorbed by the system, the change is **endothermic**, if the system loses heat, it is an **exothermic** change.

Exercise 8.2 : Calculate the amount of heat produced from the combustion of 1.6g of methane which burns in oxygen according to the following equation :



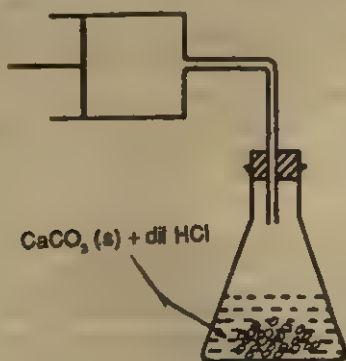
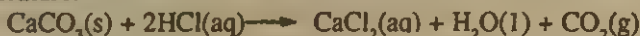
Is this reaction endothermic or exothermic ?

Solution : 16g CH_4 on combustion gives 2100 kJ heat. Therefore, 1.6g CH_4 on combustion would produce heat = $(2100/16) \times 1.6 = 210 \text{ kJ}$. Since heat is given off, $q = -210 \text{ kJ}$, has negative sign.

Reaction is exothermic i.e., heat is given off.

8.5. ENTHALPY AND ENTHALPY CHANGES

8.5.1. Meaning of Enthalpy, H : When a reaction is carried out at constant volume, the energy change is designated by ΔE . However, we generally carry out reactions at constant pressure i.e., at atmospheric pressure. Consider the energy change associated with the reaction between calcium carbonate and dilute hydrochloric acid at the room temperature.



If the reaction is carried out at constant pressure, e.g., in the apparatus shown in Fig. 8.7, then the gas carbon dioxide evolved does work against the atmospheric pressure by pushing the piston outward. In the form of work, equivalent energy is transferred to the surroundings.

Fig. 8.7. Reaction at constant pressure

Thus, ΔE which we measure will not be a true representation of the internal energy change, because some energy is being used up in doing this mechanical work. We have to take into account also the energy associated with this mechanical work. If the reaction proceeds with decrease in volume, the work is done by the surroundings and in the process the energy equivalent of this pressure-volume work is transferred to the system. To handle such situations another property known as **enthalpy**, H , is associated with every substance. The enthalpy, H , of a substance is defined as the sum of the internal energy and pressure - volume, PV energy associated with it, i.e.,

$$H = E + PV \quad (8.4)$$

Let us consider that under conditions of constant pressure, P and temperature, T a system absorbs q_p calories of heat, its volume increases by ΔV and internal energy increases by ΔE . We further assume that work other than pressure - volume work performed is zero, then from equation 8.4 we have

$$\Delta H = \Delta E + P \Delta V \quad (8.5)$$

If heat absorbed at constant pressure and constant temperature is q_p , then

$$q_p = \Delta E + P \Delta V \quad (8.6)$$

$$\text{or } q_p = \Delta H \quad (8.7)$$

i.e., heat absorbed, q_p , under conditions of constant pressure and temperature is a measure of change in enthalpy, ΔH of the system.

8.5.2. Enthalpy Change, ΔH

A compound has a definite amount of energy stored in it which is called its enthalpy or heat content* symbolized by H . It is not possible to measure enthalpy of a substance, but the enthalpy change, ΔH , which it undergoes in a physical or chemical change can be measured. The energy change at a constant pressure and temperature is called the enthalpy change, ΔH , it is equal to the amount of heat exchanged with surroundings at a constant pressure and a constant temperature. While studying the enthalpy change for a reaction, the apparatus is well insulated and temperature is allowed to change. Then the products are brought back to the temperature of the experiment - and heat exchange involved in this process is also taken into account. Though the absolute value of enthalpy, H , cannot be measured, yet it is possible to measure the enthalpy change associated with a chemical reaction. This represents the difference between the enthalpies of the products and the reactants.

$$(8.8)$$

$$\Delta H = \sum H_{(\text{products})} - \sum H_{(\text{reactants})}$$

8.5.3. Standard States, Symbols and Sign Conventions

The enthalpy change depends upon various factors and to com-

* Heat content of an element or compound depends upon pressure and temperature. To compare change in heat content, ΔH , the temperature and pressure must be identical. For this purpose a standard state is defined, when enthalpy change is measured at 298 K and 1 atm pressure, the substances are said to be in the standard state.

pare the ΔH values of different substances or reactions some standard conditions must be maintained and certain conventions should be followed. The most important of these are given below :

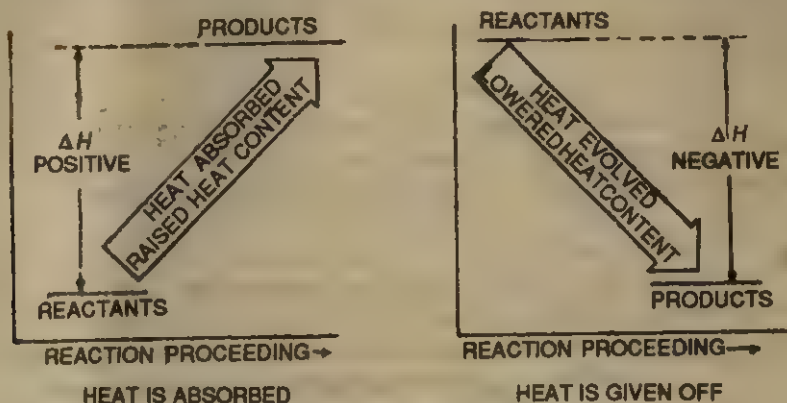
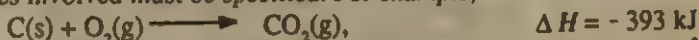


Fig. 8.8. Enthalpy changes

(i) **Amount of substance** : Each substance has a definite amount of energy stored into it, thus the energy transferred will depend upon the amount of the substance which reacts. Therefore, the quantities of substances involved must be specified. For example,



here one mole C(s) combines with one mole $\text{O}_2(\text{g})$ and forms 1 mole $\text{CO}_2(\text{g})$ with the evolution of 393 kJ of heat.

(ii) **Temperature** : For the comparison of ΔH values the standard temperature taken is 298 K (the choice of this temperature is quite arbitrary).

(iii) **Pressure** : One atmosphere pressure is taken as standard pressure to quote enthalpy values.

Symbols

Enthalpy changes measured under standard conditions are denoted by ΔH° .

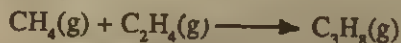
State Symbols : It is very necessary to mention the state of substances taking part in the reaction as change in state may involve a considerable amount of heat exchange. This is being done by writing within brackets s, l or g for solid, liquid or gaseous states respectively against the symbol or formula of the substance.

Sign Conventions : When in a change heat is absorbed the change is called endothermic and for this ΔH is positive since the heat content of products is more than that of reactants. ΔH is negative for changes in which heat is evolved.

Exercise 8.3 : In the reaction, $\text{CO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)}$, 335 kJ heat is evolved. What is the value of ΔH ?

Solution : Since the reaction takes place with the evolution of heat, heat content of products would be less than that of the reactants. Thus, $\Delta H = -335 \text{ kJ}$

Exercise 8.4 : What is the enthalpy change for the reaction at 298 K and 1 atm ?



ΔH_f° values for $\text{CH}_4\text{(g)}$, $\text{C}_2\text{H}_4\text{(g)}$ and $\text{C}_3\text{H}_8\text{(g)}$ are -75, +52 and -99.8 kJ mol⁻¹ respectively. Is this reaction exothermic?

Solution : $\Delta H = \Delta H_f^\circ \text{C}_3\text{H}_8\text{(g)} - [\Delta H_f^\circ \text{CH}_4\text{(g)} + \Delta H_f^\circ \text{C}_2\text{H}_4\text{(g)}]$

$$= -99.8 - [-75 + 52]$$

$= -76.8 \text{ kJ}$. As the reaction proceeds with the evolution of heat, this is an exothermic reaction.

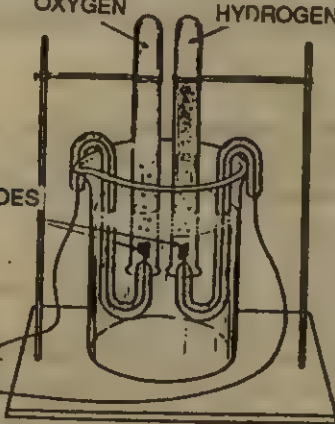
8.5.4. Conservation of Energy in a Chemical Reaction

OXYGEN

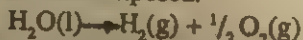
HYDROGEN

ELECTRODES

SOURCE OF ELECTRICAL DIRECT CURRENT



On passing electric current through acidulated water, it is decomposed.



On measuring the current and voltage for the decomposition of one mole of water, it is found that 286.4 kJ of electric work has been done. The net result can be written as;

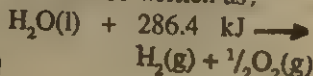


Fig. 8.9. Electrolytic decomposition of water.

Now if the heat evolved is measured when 1 mole of $\text{H}_2\text{O(l)}$ is formed from $\text{H}_2\text{(g)}$ and $\frac{1}{2}\text{O}_2\text{(g)}$, an equivalent amount of heat, i.e., 286.4 kJ is evolved. $\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{H}_2\text{O(l)} + 286.4 \text{ kJ}$. Figure 8.10 clearly shows how energy is conserved in a chemical reaction.

Energy is always conserved : *Energy in a chemical reaction can neither be created nor destroyed*, though it can be transformed from one form to another. This is called the 'law of conservation of energy'.

8.5.5. Origin of Enthalpy Change in a Reaction

Here only gaseous reactions are considered because they are simple and do not involve interactions with solvent molecules as in the case of reactions in solutions nor they involve molecular interactions of the magnitude as in solids.

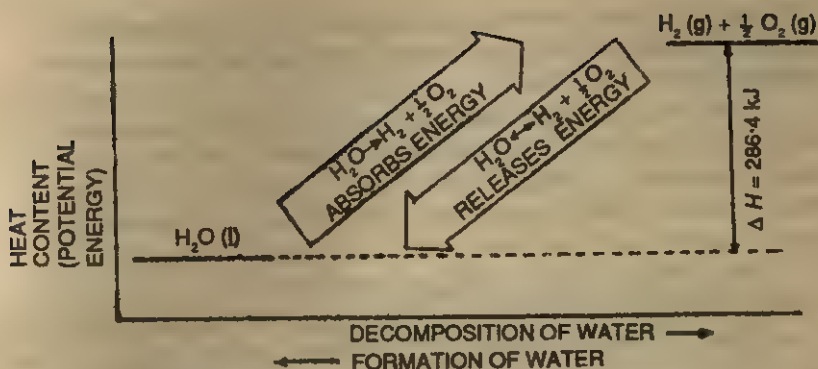
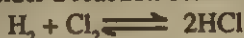
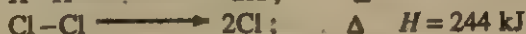
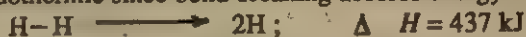


Fig. 8.10. Energy change in a chemical reaction.

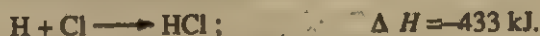
Let us consider a reaction between H_2 and Cl_2 in gas phase.



The reaction involves breaking of H - H and Cl - Cl bonds, both these processes are endothermic since bond breaking absorbs energy.



To break 1 mole H_2 and 1 mole Cl_2 energy required is $437 + 244 = 681 \text{ kJ}$. HCl is formed by the formation of a new bond between H and Cl.

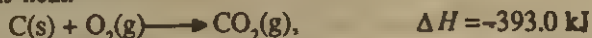


Bond formation releases energy : Energy released for the formation of 2 moles of HCl is $2 \times -433 \text{ kJ}$ i.e., -866 kJ . Net energy change in the reaction is $\Delta H = (437 + 244) - 866 = -185 \text{ kJ}$.

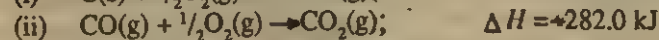
8.6. HESS' LAW OF CONSTANT HEAT SUMMATION

Since enthalpy is a state function, the value of ΔH for a chemical reaction does not depend on the path followed by the reactants to get converted into products. Let us consider, for example, the formation of one mole carbon dioxide, which can be made in two different ways.

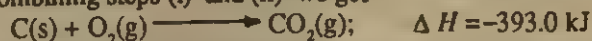
1. Carbon burns in air to form carbon dioxide with the evolution of 393 kJ heat.



2. Carbon dioxide can also be obtained in the two steps, as follows



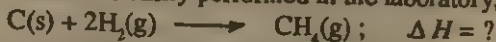
On combining steps (i) and (ii) we get



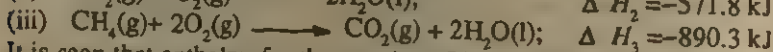
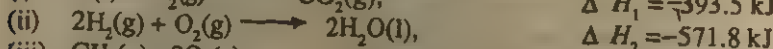
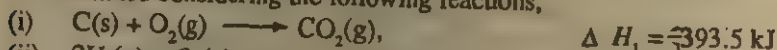
Here we find that the overall heat evolved in the formation of $CO_2(g)$ is the same whether the route 1 or route 2 is followed. On the basis of these experiments a Russian chemist, G.H. Hess enunciated a law (1840) known as Hess' law of constant heat summation which states,

"The enthalpy change (whether heat is absorbed or evolved) for a chemical reaction is the same whether the reaction takes place in one step or in several steps".

Hess' law is a direct consequence of the law of conservation of energy. It is very useful as it provides a method of determining the heat of reactions by simple addition and subtraction. Using this method, heat of those chemical reactions can be easily ascertained which cannot be easily performed in the laboratory, for example,



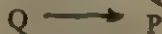
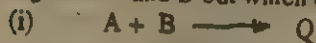
carbon and hydrogen do not react readily. ΔH for this reaction can be calculated considering the following reactions,



It is seen that enthalpy for the reaction, $\text{C(s)} + 2\text{H}_2(\text{g}) \longrightarrow \text{CH}_4(\text{g})$ can be calculated by adding (i) and (ii) and then subtracting (iii),

$$\begin{aligned} \Delta H &= \Delta H_1 + \Delta H_2 - \Delta H_3 \\ &= -393.5 + (-571.8) - (-890.3) \text{ kJ} \\ &= -75 \text{ kJ} \end{aligned}$$

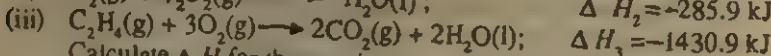
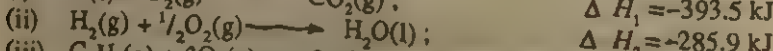
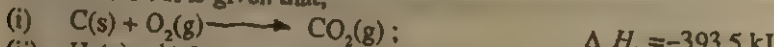
Exercise 8.5 : Consider two reactions, both of which produce P starting with A and B but which differ by the intermediate formed :



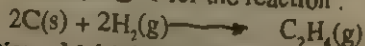
Will the enthalpy change for reaction(i) be the same as the enthalpy change for the reaction (ii) ?

Solution : Yes. The enthalpy change, ΔH , does not depend upon the path followed, provided initial and final states are the same.

Exercise 8.6 : It is given that,



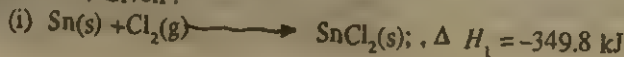
Calculate ΔH for the reaction :

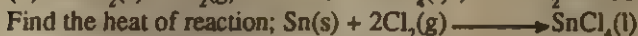


Solution : Multiply equations (i) and (ii) by 2 and add. On subtracting equation (iii) from the sum, we get,

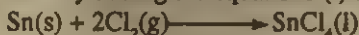
$$\begin{aligned} 2\text{C(s)} + 2\text{H}_2(\text{g}) &\longrightarrow \text{C}_2\text{H}_4(\text{g}) \\ &= 2 \times \Delta H_1 + 2 \times \Delta H_2 - \Delta H_3 \\ &= [2 \times (-393.5) + 2 \times (-285.9) - (-1430.9)] \\ &= 72.1 \text{ kJ} \end{aligned}$$

Exercise 8.7 : Given :





Solution : By adding the equations (i) and (ii)



$$\begin{aligned} \text{or} \quad \Delta H &= \Delta H_1 + \Delta H_2 \\ &= -349.8 - 195.4 \\ &= -545.2 \text{ kJ} \end{aligned}$$

8.7. HEAT OF REACTION

When chemical reactions take place they are accompanied with either the absorption or evolution of energy. The amount of energy evolved or absorbed depends upon the quantities of the reactants. Burning of 1 g coal produces less heat in comparison to the heat produced by burning of 1 kg of coal. 5 g $\text{NH}_4\text{NO}_3(s)$ on dissolution in 1 litre water would produce less cooling compared to the cooling due to 50g $\text{NH}_4\text{NO}_3(s)$ dissolved in the same volume of water. Thus heat of a reaction is defined as the amount of heat evolved or absorbed (enthalpy change) when the stoichiometric quantities of reactants as represented in a balanced chemical equation change into products. If a chemical equation also takes into account the heat change it is called a *thermochemical equation*. For example, we can write a thermochemical equation for the formation of water as,



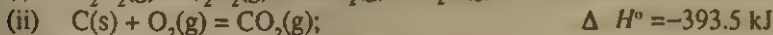
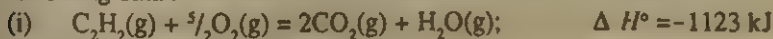
Here when one mole $\text{H}_2(g)$ combines with 0.5 mole $\text{O}_2(g)$ to form one mole $\text{H}_2\text{O}(l)$, heat evolved is 286 kJ, which is the heat of the above reaction.

Heat of reaction depends upon :

- the quantities of the reacting substances,
- the states of reactants and products,
- the temperature of the reaction,
- whether the reaction is carried out at constant volume or at constant pressure.

When a chemical reaction takes place, the energy released is not always in the form of heat. The nature of energy released depends upon the conditions of the reaction. For example, ignition of H_2 and O_2 mixture releases energy in the form of heat, light and mechanical work. When the same reaction is carried out in a fuel cell, the energy released is in the form of electricity.

Exercise 8.8 : Find ΔH_{298}° of formation of ethyne using the following data :



Solution : From the reaction (i) we have,

$$\Delta H = 2 \times \Delta H_f^\circ \text{CO}_2(\text{g}) + \Delta H_f^\circ \text{H}_2\text{O}(\text{g}) - \Delta H_f^\circ \text{C}_2\text{H}_2(\text{g}) - \frac{5}{2} \Delta H_f^\circ \text{O}_2(\text{g})$$

Substituting the values of ΔH_f° , we have,

$$-1123 = 2 \times -393.5 + -241.8 - \Delta H_f^\circ \text{C}_2\text{H}_2(\text{g}) - 5 \times 0$$

$$\Delta H_f^\circ \text{C}_2\text{H}_2(\text{g}) = 94.2 \text{ kJ mol}^{-1}$$

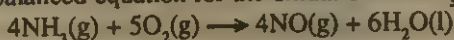
Exercise 8.9 : Calculate the standard enthalpy change, ΔH , for the oxidation of ammonia $\text{NH}_3(\text{g})$ to form nitric oxide, $\text{NO}(\text{g})$, and water, $\text{H}_2\text{O}(\text{l})$, from the following data:

Compound	$\text{NO}(\text{g})$	$\text{H}_2\text{O}(\text{l})$	$\text{NH}_3(\text{g})$
$\Delta H_f^\circ (\text{kcal mol}^{-1})$	21.52	-68.10	-11.12

Solution : The enthalpy change, ΔH° refers to the change in heat content between the products and the reactants for a reaction in which each reactant and product is in its standard state.

$$\Delta H_{\text{reaction}} = \sum \Delta H_{f(\text{products})} - \sum \Delta H_{f(\text{reactants})}$$

The balanced equation for the oxidation of NH_3 is



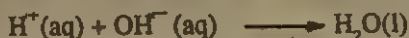
$$\begin{aligned} \Delta H_{\text{reaction}} &= [4(\Delta H_f^\circ \text{NO}(\text{g})) + 6(\Delta H_f^\circ \text{H}_2\text{O}(\text{l})) \\ &\quad - 4(\Delta H_f^\circ \text{NH}_3(\text{g})) - 5(\Delta H_f^\circ \text{O}_2(\text{g}))] \\ &= [4(21.52) + 6(-68.10) - 4(-11.12) - 5(0)] = \\ &\quad -278.04 \text{ kcal} \end{aligned}$$

-278.04 kcal is the heat of the reaction as expressed by the balanced chemical equation in which 4 moles of $\text{NH}_3(\text{g})$ are oxidized. Thus for 1 mole of $\text{NH}_3(\text{g})$ it will be

$$\frac{-278.04}{4} = -69.51 \text{ kcal mol}^{-1}$$

8.7.1. Heat of Neutralization

You have learned about the neutralization reactions. Reaction between an acid and a base is referred to as neutralization and it is always accompanied with the evolution of heat. The heat of neutralization is defined as the amount of heat evolved when 1 g equivalent of an acid combines with 1 g equivalent of a base in a dilute solution.* Heat of neutralization can also be defined as the amount of heat evolved when 1 mole of water is formed from the reaction between an acid and a base in dilute solution. The neutralization reaction is essentially,



From the experimental observations, it is evident that heat of neutralization of most of the strong acids and strong bases is always 57.1 kJ. However, the heat of neutralization of a strong acid and a weak base

* By dilute solution we mean that there is no enthalpy change on further dilution of the solution.

or a weak acid and a weak base or a weak acid and a strong base is always less than 57.1 kJ. It is considered that this difference of energy (-57.1 kJ. - heat of neutralization) is used up in the dissociation of the weak acid or the base.

Exercise 8.10 : Considering the heat of neutralization equal to 57.1 kJ, find out heat of neutralization of the following reaction :

- (i) 0.2 mole of HCl combine with 0.2 mole of NaOH,
- (ii) 250 cm³ of 2M H₂SO₄ combine with 500 cm³ of 1M NaOH.

Solution : (i) As the normality of HCl and NaOH are the same as their molarity, we know,

1 g equivalent of an acid combines with 1 g equivalent of a base to give 57.1 kJ heat.

0.2 g equivalent of an acid combine with 0.2g equivalent of base will give 57.1 × 0.2 kJ heat = 11.4 kJ, $\Delta H = -11.4$ kJ.

- (ii) In 250 cm³ of 2M H₂SO₄, number of g equivalent

$$= \frac{2 \times 2 \times 250}{1000} = 1 \text{ g equivalent}$$

In 500 cm³ of 1 M NaOH, number of g equivalent

$$= \frac{500 \times 1}{1000} = 0.5 \text{ g equivalent}$$

In this case, 0.5 g equivalent of NaOH will neutralise 0.5 g equivalent of H₂SO₄ leaving rest of the H₂SO₄ unreacted.

$$\begin{aligned} \text{Heat evolved} &= 57.1 \times 0.5 \\ &= 28.5 \text{ kJ} \end{aligned}$$

$$\text{or } \Delta H = -28.5 \text{ kJ}$$

8.7.2. Heat of Combustion

Combustion reactions are those which are accompanied with the evolution of large amount of heat and light energy. These reactions are very useful for the survival of the mankind. While combustion of food directly provides heat energy to the body, combustion energy of fuels are utilised for all types of comforts of the mankind. Heat of combustion is defined as "the amount of heat evolved when 1 mole of a substance is burned completely in excess of oxygen". For example, heat of combustion of carbon is 394 kJ mol⁻¹. Heat of combustion of some of the substances is given in Table 8.1.

TABLE 8.1. Heat of combustion

Substance	Heat of combustion (kJ mol ⁻¹)	Substance	Heat of combustion (kJ mol ⁻¹)
C (s)	- 394	C ₂ H ₅ OH (l)	- 1391
H ₂ (g)	- 286	Glucose (s)	- 2900
CH ₄ (g)	- 890.3	Benzoic acid (s)	- 3536
C ₂ H ₄ (g)	- 1324	Phenol (s)	- 3200

Exercise 8.11 : Calculate the amount of heat evolved when 100 g each of carbon, butane and benzoic acid are burned in excess of oxygen. (Heat of combustion of C (s) = 394, butane = 2600 and benzoic acid = 3536 kJ per mole).

Solution : 1 mole of C = 12 g of C

12 g of C produces heat = 394 kJ

100 g of C will produce heat = $\frac{394 \times 100}{12} = 3283 \text{ kJ}$

100 g of butane will give heat = $2600 \times 100/58 = 4482 \text{ kJ}$

100 g of benzoic acid will give heat = $3536 \times 100/122 = 2898 \text{ kJ}$.

Exercise 8.12 : (i) A cylinder of LPG contains fuel equivalent to 14.2 kg of butane. If a family needs 40,000 kJ energy per day for cooking, how long the cylinder will last ?

(ii) If air supply to the burner is defective which results in a 13% wastage of fuel, how long the cylinder last? (Heat of combustion of butane is 2600 kJ).

Solution : (i) Total amount of heat produced by the gas in the cylinder = $14.2 \times 2600 \times 1000/58 = 6,36,551 \text{ kJ}$

Number of days the cylinder will last = $\frac{636551}{40000} = 16 \text{ days}$

(ii) At 13% wastage, heat produced will be = $\frac{636551}{100} \times \frac{87}{100} = 553800 \text{ kJ}$

Number of days the cylinder will last = $\frac{553800}{40000} = 13.8 \text{ days}$

8.7.3. Heat of Formation

In a chemical reaction, elements and compounds are converted into another compound and this process will either absorb or release energy. The heat of formation of a substance is defined as the amount of heat evolved or absorbed in the formation of 1 mole of that substance from its elemental constituents. Heat of formation is represented as ΔH_f .

It is the standard convention that heat of formation of elements in their standard states is always taken as zero. In thermochemical conversions, the standard state of a substance is taken at 298K and 1 atm pressure. Thus, standard heat of formation (ΔH_f°) of a substance will be its heat of formation at 1 atm and 298K. Standard heat of formation of certain substances are given in Table 8.2.

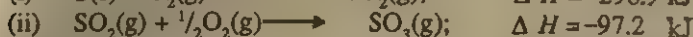
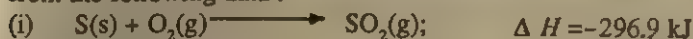
TABLE 8.2. Standard heat of formation

Substance	ΔH_f° (kJ mol ⁻¹)	Substance	ΔH_f° (kJ mol ⁻¹)	Substance	ΔH_f° (kJ mol ⁻¹)
H ₂ O(l)	-286	CH ₄ (g)	-75	HNO ₃ (l)	-173
H ₂ O(g)	-242	C ₂ H ₆ (g)	-85	NaCl(s)	-411
HF(g)	-269	C ₂ H ₄ (g)	+52	Al ₂ O ₃ (s)	-1670
HCl(g)	-92	C ₂ H ₂ (g)	+227	CaSO ₄ (s)	-1430

Heat of formation, ΔH_f° , is very useful in calculating the heat of reaction ΔH .

$$\Delta H_{\text{(reaction)}} = \sum \Delta H_f^\circ \text{(products)} - \sum \Delta H_f^\circ \text{(reactants)} \quad \dots\dots(8.9)$$

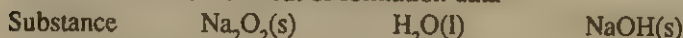
Exercise 8.13 : Calculate the heat of formation of H₂SO₄(l) at 298K from the following data :



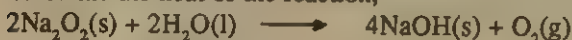
Solution : Adding equations (i) to (iv), we obtain



Exercise 8.14 : Given heat of formation data



Calculate the heat of the reaction,



$$\Delta H_{\text{(reaction)}}^\circ = \sum \Delta H_f^\circ \text{(products)} - \sum \Delta H_f^\circ \text{(reactants)}$$

Substituting the value of ΔH_f°

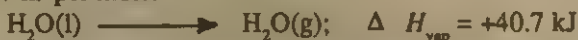
$$\begin{aligned} &= [4 \times \Delta H_f^\circ \text{NaOH(s)} + \Delta H_f^\circ \text{O}_2\text{(g)}] \\ &\quad - [2 \times \Delta H_f^\circ \text{Na}_2\text{O}_2\text{(s)} + 2 \times \Delta H_f^\circ \text{H}_2\text{O(l)}] \\ &= [4 \times (-426.8) + 0] - [2 \times (-504.6) + 2 \times (-286.0)] \\ &= -1707.2 + 1581.2 \\ &= -126.0 \text{ kJ} \end{aligned}$$

8.7.4. Heat of Fusion and Vaporization

A substance can exist in solid, liquid or gaseous phase. Ice easily melts at room temperature into liquid, and liquid water can be easily evaporated into gas phase. These state conversions are always accompanied by either evolution or absorption of heat. A solid can be converted into liquid phase by the absorption of heat. The process is also referred to fusion.

Heat of fusion of a substance is the amount of heat absorbed when 1 mole of the solid is converted into liquid at a constant temperature (melting point). Heat of fusion of ice is 6.01 kJ per mole.

Heat of vaporization of a substance is the amount of heat absorbed when 1 mole of the liquid is converted into gas phase at a constant temperature (boiling point). Heat of vaporization of water is 40.7 kJ per mole.



For a substance, the enthalpy of vaporization is higher as compared to that of fusion. This is because of the weaker attractive forces involved in the gaseous state.

8.8. SOURCES OF ENERGY

Energy is a vital requirement to improve agricultural production, turn the wheel of industry, provide goods and services throughout the nation, and to improve the quality of life of our people. The science tells that we cannot create energy, then from where we get the energy? There are various types of sources of energy. The energy can be easily harnessed from the sun, air, water and earth. The earth contains a large amount of substances which can be used as sources of energy. The chemical substances which provide energy by the process of combustion are referred to fuel. The fossil fuels - coal and petroleum, were formed from the remains of the extinct vegetable life below the earth crust under the high temperature and pressure conditions. The entire coal requirements are met from indigenous production which was 114 million tonnes in the beginning of the decade 1980-1990. Indigenous production of petroleum is stepped up and today more than 50% need of the country is fulfilled from within.

We can classify the various sources of energy into :

- (i) Commercial and non-commercial
- (ii) Fossil and renewable.

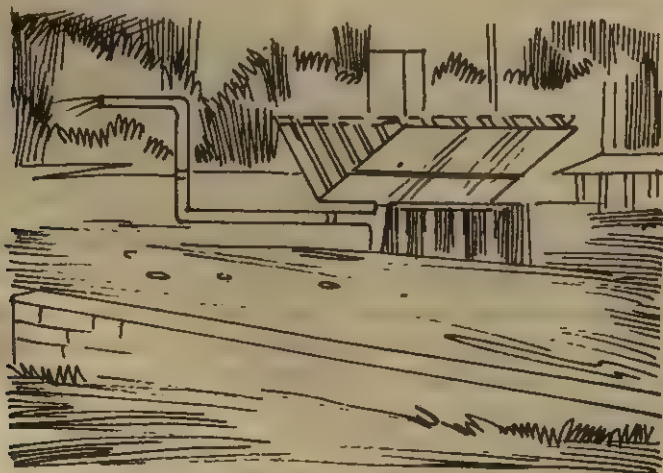


Fig. 8.11. Solar thermal water pump.

Apart from fossil fuel, the commercial sources of energy include hydroelectric and nuclear power. This forms about 60% of the total energy consumption. The remaining 40% of energy is obtained by non-commercial sources which include firewood, agricultural waste and animal dung. This type of energy sources are very popular among village folks who constitute 80% population of the country.

In recent years, there has been a major and sustained effort to expand indigenous commercial sources of energy as well as to rapidly develop the new and renewable sources of energy. The new sources of energy include solar, biomass, wind, electrochemical storage, geothermal, hydrogen and ocean (tidal) energy.

India has a significant level of solar insolation over wide regions. The total solar energy received by us is 6×10^{14} MWH annually. This is about 10^6 times the entire requirement of our country. Though solar energy is abundantly available but it is diffused and intermittent. The appropriate collection and storage of this energy will help us to solve our energy problems. Presently only a small amount of solar energy is harnessed by the use of solar cookers, solar stills, solar water heating systems, solar crop dryers, solar pumps, solar power plants and solar cold storages. Some of these systems use solar cells which directly convert solar energy into electrical energy.

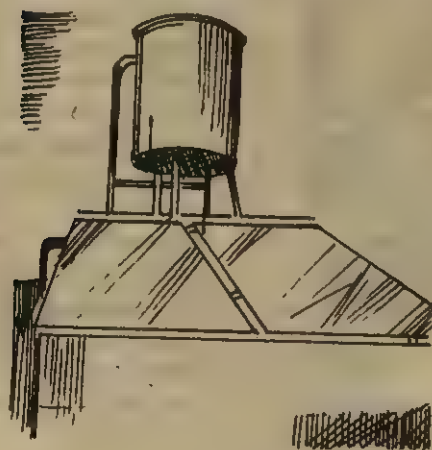


Fig. 8.12. Domestic solar water heater.

Wind energy is another renewable energy source. Though the speed of wind is low in most parts of the country, the wind mills which can operate at low wind speed have been developed and traditionally used in the past. Wind mills extract kinetic energy from the wind and convert it into useful shaft power. The wind mills are commonly used for

grain grinding, fodder cutting, water pumping and for generating electricity.

Bioenergy is available as biomass and biogas. Biomass is produced as a result of solar energy conversion through photosynthesis. It can directly be used as a fuel or can be easily converted into liquid or gase-

ous fuels. Biogas is produced from animal dung, sewage, crop residue, vegetable wastes, poultry droppings, pig manure *etc.* Only from cow dung $2.2 \times 10^{10} \text{ m}^3$ of biogas can be produced annually.



Fig.8.13 Water pumping wind mill



Fig.8.14. Family type biogas plant

adopted are :

1. more efficient combustion of fuels
2. waste heat recovery
3. total energy system concept
4. recycling of raw materials
5. effective utilisation of by-product fuels
6. efficient heating methods and appliances

Nuclear power is another major area which will be a big source of energy for tomorrow. Nuclear fission and fusion reactors are very important. India entered in the field of nuclear energy by commissioning the plant at Tarapore. We have also stalled nuclear plants at Katakamm and Narora. India believes in the peaceful uses of nuclear energy and more emphasis is in the form of electric energy and in the medicine. Nuclear torches are used to cure the most dreadful disease - cancer.

Apart from developing new sources of energy, it is also essential to conserve energy. Some of the methods which can be

7. development of more efficient energy conversion techniques
8. improvement in the existing designs of auto-machines, electric motors *etc.*

The consumption of energy also reflect upon the quality of life in the country. Though we are a developing country, but in the utilisation of energy, we are far behind even from the small and underdeveloped countries. The per capita utilisation of energy of some of the countries is given in Table 8.3

TABLE 8.3. Consumption of electrical energy in India compared with consumption in a few other countries

Country	Estimated electrical energy consumption per person per year in (KWH/person/year) (1984-85)
India	220
China	340
Singapore	3500
Great Britain	4700
USSR	5100
Japan	5200
USA	14500

8.9. CRITERIA FOR SPONTANEOUS CHANGE

Spontaneous processes are those which naturally occur without the aid of any external agency. Flow of water from higher level to lower level, flow of heat from higher temperature to lower temperature, evaporation of water, melting of ice, dissolution of sugar in water and combination of hydrogen and chlorine in sunlight to give HCl(g) are spontaneous reactions in nature. On the other hand there are a large number of physical and chemical changes which need some external energy so that the change can take place, *e.g.*, reaction between the $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$, decomposition of KClO_3 , formation of SO_2 at room temperature *etc.* These changes are non-spontaneous.

Let us have a close look at some of the spontaneous processes. Consider reaction between aluminium and bromine. As soon as the two come in contact, the chemical change takes place with the evolution of heat. Same thing happens when sodium or potassium is brought in contact with water. These reactions are exothermic in nature; *i.e.*, heat is evolved during the change. Now what is the relation between the enthalpy or heat content of the reactants and the products.

The energy considerations reveal that heat content of products is less than that of the reactants. Thus, one can safely say that the reactions in which enthalpy of products is less than that of reactants will be spontaneous. Is it the sufficient condition for spontaneous process? The answer is no, because, in nature, there are several reac-

tions which are endothermic in nature yet spontaneous. In an endothermic reaction, heat is absorbed, therefore, the heat content of product will be more than that of the reactants. Evaporation of water, dissolution of NH_4Cl in water and melting of ice are endothermic reactions but are spontaneous in nature. In solid ice, the arrangement of molecules follow a certain order and relative position of H_2O molecules are almost fixed. In liquid water, the molecules exchange their positions quite frequently but still for a small duration their positions are somewhat fixed. However, in the vapour phase, the water molecules change their positions at a very high rate as these are constantly moving at high speed. How can one differentiate the various states?

In routine life, we all appreciate an arranged house, a properly arranged library, a pack of new rupee notes, a well looked garden etc. This is because the systems have order or symmetry. A pack of old notes partly torn or mutated are not liked because of disorder or randomness. But human liking and spontaneous reactions have different attitude towards randomness. A spontaneous reaction which proceeds with the absorption of energy, e.g., melting of ice and evaporation of water, is always associated with more random arrangements. Thus, we can say that vapours of water possess more disorder than the water which in turn is more disordered when compared with ice. Thus an endothermic spontaneous reaction is always associated with more randomness or disorder.

Disorder or randomness of a system is measured in terms of entropy. It is denoted by 'S' and is a state function. Though it is not possible to find absolute value of entropy, the change in entropy, ΔS , during a reaction can be easily ascertained.

$$\Delta S = \sum S_{(\text{products})} - \sum S_{(\text{reactants})} \quad (8.10)$$

From the on going discussion, it is evident that a spontaneous reaction must follow two criteria : (i) decrease in the enthalpy and (ii) increase in the disorder or entropy. The enthalpy changes are measured in the units of joule while the entropy changes are measured in the unit of JK^{-1} . The entropy change of an isothermal system can be correlated with the amount of heat supplied or withdrawn. If ΔQ is the amount of heat supplied to an isothermal system at the temperature $T\text{K}$, the entropy change will be given by

$$\Delta S = \frac{\Delta Q}{T} \quad (8.11)$$

How does entropy change in different systems?

Even a visual examination of system during the change can provide the answer to this question. A generalisation can be made using the following concepts :

1. Conversion of solid into liquid, liquid into gas or solid into gas increase the entropy while reverse changes decrease the entropy.

2. In a homogeneous reaction, increase in the number of moles of products results in an increase in entropy while decrease in number of moles decreases entropy.

3. Mixing of two or more substances into a homogeneous state always increases entropy.

We have seen that a spontaneous reaction is accompanied with decrease in enthalpy and increase in entropy. J.W. Gibbs studied the role of these concepts on the spontaneity of reactions. He introduced a new concept named as free energy and denoted by G . The free energy is also a state function and it is related with enthalpy and entropy using the relation,

$$G = H - TS \quad (8.12)$$

It is easy to determine free energy change for a reaction at constant temperature

$$\Delta G = \Delta H - T \Delta S \quad (8.13)$$

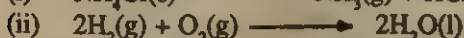
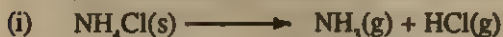
Gibbs suggested that a spontaneous reaction always results a decrease in free energy. Alternatively, we can say that a change will take place spontaneously only when free energy flows from higher level to lower level. Thus, if, e.g., $\Delta G > 0$, the reaction will not take place while for $\Delta G < 0$, the reaction will spontaneously occur. For $\Delta G = 0$, the reaction attains a state of equilibrium.

The favourable conditions at which ΔG will be negative, can be expressed in terms of enthalpy and entropy changes also. A reaction may have negative or positive values of entropy and enthalpy. But will it be spontaneous or not, can be predicted from the Table 8.4.

TABLE 8.4. Prediction of direction of reactions with different signs of ΔH and ΔS

ΔH	ΔS	ΔG	Remarks
-ve	+ve	-ve	Reaction will be spontaneous at all temperatures.
-ve	-ve	-ve if $\Delta H > T\Delta S$	(i) spontaneous at low temperatures. (ii) non-spontaneous at high temperatures.
+ve	+ve	-ve if $T\Delta S > \Delta H$	(i) spontaneous at high temperatures. (ii) non-spontaneous at low temperatures.
+ve	-ve	+ve	non-spontaneous at all temperatures.

Exercise 8.15 : Determine the sign of entropy change in the following reactions :



- (iv) $\text{CO}_2(\text{s}) \longrightarrow \text{CO}_2(\text{g})$
 (v) $\text{Li}^+ + n\text{H}_2\text{O}(\text{aq}) \longrightarrow \text{Li}(\text{H}_2\text{O})_n^+$
 (vi) Normal egg \longrightarrow hard boiled egg

Solution : (i) 1 mole of a substance in the solid state forms 2 moles of gases, hence $\Delta S > 0$. Positive

(ii) 3 moles vapours change to 1 mole liquid, $\Delta S < 0$. Negative

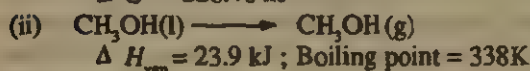
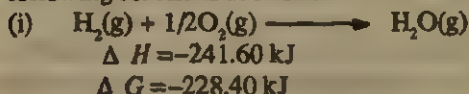
(iii) $\Delta S > 0$. Positive

(iv) $\Delta S > 0$. Positive

(v) More order, $\Delta S < 0$. Negative

(vi) More order, $\Delta S < 0$. Negative

Exercise 8.16 : Calculate the entropy change ΔS per mole for the following reactions at 298K.



Solution : We know

$$\Delta G = \Delta H - T \Delta S$$

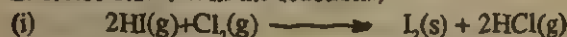
$$\text{or } \Delta S = \frac{\Delta H - \Delta G}{T}$$

(i) Substituting the values

$$\Delta S = \frac{[-241.60 - (-228.40)] \times 1000}{298} = -44.3 \text{ JK}^{-1}$$

(ii) $\Delta S = \frac{23.9 \times 10^3}{338} = 70.7 \text{ JK}^{-1}$

Exercise 8.17 : Will the reactions,



proceed spontaneously in the forward direction at 298K?

Given:

Substance $\Delta G_{\text{form}} (\text{kJ mol}^{-1})$

$\text{HI}(\text{g})$ 1.8

$\text{HCl}(\text{g})$ -95.2

H_2S -33.8

For reaction

(i) $\Delta G = 2 \times -95.2 - 2 \times 1.8$
 $= -194 \text{ kJ}$

since ΔG is negative, the reaction is spontaneous

(ii) $\Delta G = 2 \times -95.2 - (-33.8)$
 $= -156.6 \text{ kJ}$, reaction is spontaneous.

8.10 WHY THE ENERGY CRISIS IF ENERGY IS CONSERVED IN NATURE ?

As the population of the country is increasing, the sources of en-

ergy are utilised at a higher rate. This will certainly cause a crisis for the energy. The available form of fuels which supply energy to us are becoming rarer day by day. The increasing cost of coal and petrol is putting a check on the utilisation of these sources of energy. But why the crisis when energy is conserved in nature?

Let us study the energy utilisation and conservation reactions. The huge amount of coal or firewood is converted into energy when required. An average family in India utilises various sources of energy to have 40,000 joules of energy per day for cooking alone. Though large amount of energy reserves are available which were formed over a very large numbers of years in the beginning of civilisation. The burning of fuel releases carbon dioxide into air and this process is very fast. To reform this, considerable efforts are needed by the nature. In the form of photosynthesis, nature converts carbon dioxide to firewood. But this process takes much longer time. At the same time, it is a common experience that the efficiency of all the processes is always less than 100%. Conversion of coal into heat is accompanied by the discharge of light. Though energy is conserved but by these side processes, a portion of energy is always converted into those forms which cannot be recovered back. The engines based on carnot cycle utilise only 20-40% of the energy produced by burning of fuel. The efficiency of an engine which is defined as

$$\frac{\text{work done by the engine}}{\text{energy supplied to engine}}$$
 is always less than unity.

Free energy change also provides information about the maximum useful work which can be obtained from any process. The energy which cannot be converted into useful efforts is utilised to increase the entropy of universe. Energy crisis is actually resulting from the fact that whatever energy we utilise, it cannot be converted back into the same form without more expensive and less convenient methods.

SELF ASSESSMENT QUESTIONS

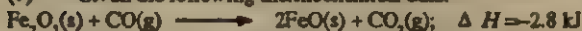
MULTIPLE CHOICE QUESTIONS

8.1. Put a (✓) mark against the most appropriate choice:

- (i) At constant volume, q equals:
(a) ΔH (b) ΔE (c) ΔG (d) $P \Delta V$
- (ii) For an adiabatic process:
(a) $P \Delta V = 0$ (b) $q = 0$ (c) $\Delta T = 0$ (d) $\Delta E = q$
- (iii) What is Δn_{gas} for the combustion of one mole of ethanol (l), when both reactants and products are at 298K?
(a) -1 (b) 0 (c) +1 (d) 2
- (iv) The combustion of 0.1 g of methane causes a temperature rise of 2.0°C in a bomb calorimeter that has a heat capacity of 500 joules/°C. What is the internal energy change per mole of methane for the combustion?

(a) +160 kJ (b) 1kJ (c) -160 kJ (d) -1 kJ

(v) Given the following thermochemical data:



ΔH in kJ for the reaction :



(a) 8.0 kJ (b) 13.6 kJ (c) -24.4 kJ (d) -13.6 kJ

(vi) Which of the following must be true for a spontaneous change?

(a) $\Delta G > 0$ (b) $\Delta H > 0$ (c) $T \Delta S < 0$ (d) $\Delta S_{\text{univ}} > 0$

(vii) Which of the following statements is incorrect ?

(a) $P \Delta V$ can have unit of joules.

(b) Energy can be transferred as heat or work

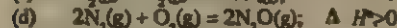
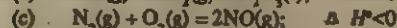
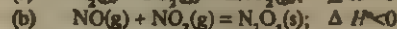
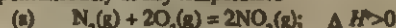
(c) In an endothermic process temperature remains constant

(d) Reactions which do not involve gases, $\Delta H \approx \Delta E$.

(viii) For a spontaneous endothermic process

(a) $\Delta H = 0$ (b) $\Delta H < 0$ (c) $\Delta S > 0$ (d) $\Delta G > 0$

(ix) Indicate which of the reactions of formation of nitrogen oxides can proceed spontaneously at any temperature

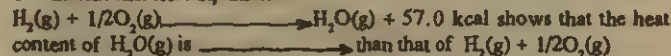


(x) What is the sign of ΔG for the process of ice melting at 263K?

(a) $\Delta G > 0$ (b) $\Delta G = 0$ (c) $\Delta G < 0$ (d) None of the above.

8.2. Fill in the blanks

(i) The thermochemical equation



(ii) The reaction $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l}) + 68.3 \text{ kcal}$ shows that the heat of combustion of hydrogen is _____ kcal mol^{-1} .

(iii) The Greek prefix for into is endo; hence reactions that _____ heat are described as endothermic reactions. During such reactions, the temperature of the reactions system will _____.

(iv) Formation of a chemical bond is a process in which heat is _____, the reaction would be an _____ reaction.

(v) The heat energy q absorbed by a gas is ΔH if _____ is kept constant.

(vi) The heat liberated or absorbed in the reaction $\text{X} \longrightarrow \text{Y}$ depends only upon the relative contents of _____ and _____ and not on whether the reaction is stepwise or _____.

(vii) Indicate the relative heat contents of A and B on the diagram given below using the information that the reaction $\text{A} \longrightarrow \text{B}$ is exothermic.



(viii) A handbook lists the reagents heat of formation of $\text{NH}_3(\text{g})$ as -40 kJ mol^{-1} . For the reaction



ΔH is _____

- (ix) When one mole of water changes into steam at 373K, and 1 atm, the entropy ———.
- (x) Crystallization of sugar from its saturated solution results in the ——— of entropy.
- 8.3. Point out the correct statements of the followings.
- For any chemical reaction carried out in any manner the quantity of heat associated with the reaction is $\Delta E - w$
 - A full boiled egg has higher entropy than a half boiled egg.
 - Amorphous glass has higher entropy than crystalline glass.
 - Entropy decreases on separation of a mixture into its constituents.
 - For a reaction to occur spontaneously, ΔH must be negative.
 - The internal energy of an isolated system is constant.
 - Enthalpy is a state function.
 - The enthalpies of all the elements in their standard states at 298K are taken to be zero.
 - A gas shows cooling effect in isothermal expansion.
 - Bond breaking is an endothermic process.

8.4 Match the following choosing one item from column X and the appropriate item from column Y

Column X	Column Y
(A) ΔE	(i) Hess' law of constant heat summation
(B) $-\Delta H$	(ii) increase in disorder
(C) $q = \Delta E + w$	(iii) spontaneous reaction
(D) $\Delta H = \Delta E + \Delta nRT$	(iv) endothermic
(E) $\Delta S > 0$	(v) relationship between q_p and q_v
(F) $\Delta G < 0$	(vi) q_v
(G) $\Delta H > 0$	(vii) heat of combustion
(H) $2C(s) + H_2(g) \rightarrow C_2H_2(g); \Delta H = 17 \text{ kJ}$	(viii) exothermic
(I) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l); \Delta H = -1500 \text{ kJ}$	(ix) conservation of energy
(J) $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g); \Delta H = x$	(x) heat of formation
$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g); \Delta H = y$	
$C(s) + O_2(g) \rightarrow CO_2(g); \Delta H = x+y$	

SHORT ANSWER QUESTIONS

- 8.5 For the following reactions state : whether the tendency towards minimum energy favours reactants or products.
- $H_2O(l) \rightarrow H_2O(s); \Delta H = -7.0 \text{ kJ}$
 - $CaCO_3(s) + 162 \text{ kJ} \rightarrow CaO(s) + CO_2(g)$
 - $I_2(s) + 8.0 \text{ kJ} \rightarrow I_2(\text{in } C_2H_5OH)$
- 8.6 Classify the following into open, closed and isolated systems:
- a beaker of water being heated on a burner
 - our Universe
 - a completely thermally insulated sealed box of air.
- 8.7 The reaction, $C(\text{graphite}) \rightarrow C(\text{diamond})$ is difficult to take place. For this reaction calculate ΔH , if the heat of combustion of $H_{2(\text{diamond})}$ and $C_{(\text{diamond})}$ are -393.1 and -395.0 kJ mol⁻¹ respectively.
- 8.8 For Octane, C_8H_{18} , the heat of combustion, ΔH , is -5200 kJ. Calculate the amount of heat produced when 1.0 kg of octane burns.
- 8.9 Given the reactions
- $H_2(g) + Cl_2(g) \rightarrow 2HCl(g); \Delta H = -176 \text{ kJ}$
 - $2H_2(g) + O_2(g) \rightarrow 2H_2O(l); \Delta H = -571 \text{ kJ}$
- calculate ΔH for the reaction $4HCl(g) + O_2(g) \rightarrow 2Cl_2(g) + 2H_2O(l)$
 - calculate ΔH when one gram HCl burns.

8.10 As the temperature increases, does the entropy increase or decrease? Why?

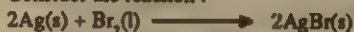
8.11. Consider the following diagram: on opening the stopper, S, gas 1 mixes with gas 2 though both gases are at the same temperature and pressure. What is the driving force?



8.12. The heat of vaporization (ΔH) of water at 378K is 9.6 kcal/mole. The entropy change is 26 cal/mole-deg. What is the free energy for the conversion of one mole of liquid water at 378K into steam?

8.13. Estimate the normal boiling point of CCl_4 . $\Delta H_{\text{vap}} = +30.0 \text{ kJ mol}^{-1}$. The molar entropies for liquid and gaseous CCl_4 are 205.0 and 298 joules/K respectively.

8.14. Consider the reaction :



For this reaction at 298K and 1 atm pressure,

$$\Delta G^\circ = -192.5 \text{ kJ}; \quad \Delta H^\circ = -201.4 \text{ kJ}.$$

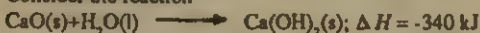
- Do you expect this reaction to be spontaneous at 298K and 1 atm pressure.
- calculate ΔS° for the reaction.
- What does the sign of ΔS indicate about the relative degree of order in the reactants and the products?

TERMINAL QUESTIONS

8.1. The internal energy of an ideal gas depends only on its temperature. A sample of an ideal gas is allowed to expand isothermally.

- Does the gas do work?
- Does the system exchange heat with the surroundings?
- Does the temperature of the gas change?

8.2 Consider the reaction



- What is the heat of reaction when 1 g CaO reacts?
- How much heat in kilojoules is evolved/absorbed with the production of 100 kg of slaked lime?

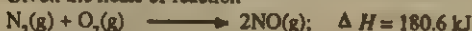
8.3 An experimental determination of ΔE for the combustion of ethanol yields a value of -23.4 kJ per gram at 298 K.

(i) What is ΔE for this reaction, in kJ/mol $\text{C}_2\text{H}_5\text{OH}$?

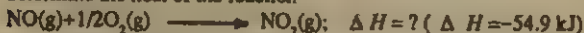
(ii) What is ΔH for this reaction?

(Ans: $\Delta E = -1076.4 \text{ kJ mol}^{-1}$, $\Delta H = -1078.9 \text{ kJ mol}^{-1}$)

8.4. Given the heats of reaction



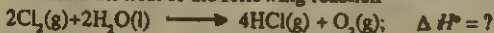
determine the heat of the reaction



8.5. (a) Why is ΔH not a good measure of the spontaneity of a reaction?

(b) How is temperature related to the spontaneity of a reaction?

8.6. Calculate the heat of the following reaction



Given

$$\Delta H_f^\circ \text{HCl}(g) = -92.30 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ \text{H}_2\text{O}(l) = -285.80 \text{ kJ mol}^{-1}$$

$$(\Delta H = 202.4 \text{ kJ})$$

8.7. Predict the sign of ΔS for

- dissolving tea in water
- the crystallization of salt from brine
- $\text{I}_2(s) \longrightarrow \text{I}_2(g)$
- $\text{Br}_2(l) + 3\text{F}_2(g) \longrightarrow 2\text{BrF}_3(l)$
- $\text{TiCl}_4(g) + 2\text{Mg}(s) \longrightarrow \text{Ti}(s) + 2\text{MgCl}_2(s)$

8.8. Given the following standard heats of reactions:

- heat of formation of water = -68.3 kcal,

(ii) heat of combustion of acetylene = -310.6 kcal,

(iii) heat of combustion of ethylene = -337.2 kcal,

Calculate the heat of reaction for the hydrogenation of acetylene

at constant volume at 298K. (Ans. $\Delta E = -41.1$ kcal) (IIT 1984)

- 8.9. The bond dissociation energies of gaseous H_2 , Cl_2 and HCl are 104, 58 and 103 kcal/mole respectively. Calculate the enthalpy of formation of HCl

(Ans: -22 kcal mol⁻¹)

- 8.10. Which of the following processes are spontaneous?

(i) the decomposition of $H_2O_2(l)$ into the elements at 298K and 1 atm
($\Delta G_f^\circ(H_2O_2(l)) = -104$ kJ)

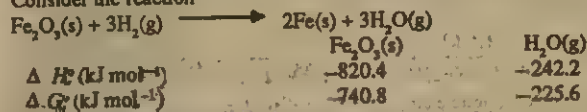
(ii) the expansion of a gas in vacuum

(iii) the freezing of water at 273 K and 1 atm.

- 8.11. (a) Give examples of several forms of energy.

(b) Give examples of systems that convert one energy form into another.

- 8.12. Consider the reaction



(i) Is the above reaction spontaneous at 800K and 1 atm.

(ii) Calculate the temperature at which the reaction is at equilibrium at one atm. (Ans 938 K)

- 8.13. Calculate the free energy change for the formation of water gas at 298K. The enthalpy and entropy changes are 31.380 kcal mol⁻¹ and 32 cal K⁻¹ respectively. Also calculate the free energy change at 1000°C. Predict at which temperature the reaction is feasible,

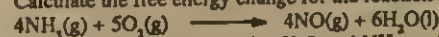
(Ans. ΔG at 298K = 91.4 kJ mol⁻¹, ΔG at 1000°C = -39.1 kJ mol⁻¹ Reaction is feasible at 1000°C).

- 8.14. Calculate the melting point of potassium chloride from the following data :

$$\Delta H = 7.25 \text{ kcal mol}^{-1}, \Delta S = +0.00673 \text{ kcal K}^{-1} \text{ mol}^{-1}$$

(Ans. T = 1080K)

- 8.15. Calculate the free energy change for the reaction at 298K and 1 atm.



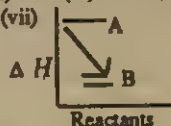
The absolute entropies of NO , H_2O and NH_3 are 20.7, -56.7 and -4.0 kcal K⁻¹ mol⁻¹ respectively.

(Ans. 1010.0 kJ mol⁻¹)

ANSWERS TO SELF ASSESSMENT QUESTIONS

- 8.1 (i) (b) (ii) (b) (iii) (a) (iv) (c) (v) (c) (vi) (d) (vii) (c) (viii) (c) (ix) (c) (x) (a)

- 8.2 (i) less (ii) 68.3 (iii) absorb, decrease (iv) evolved, exothermic (v) pressure (vi) X, Y, direct (vii)



(viii) +80 kJ

(ix) increases

(x) decrease.

- 8.3. (i) (F) (ii) F (iii) T (iv) T

(v) F (vi) T (vii) T

(viii) T (ix) F (x) T

- 8.4. (A) (vi) (B) (viii); (C) (ix) (D) (v) (E) (ii); (F) (iii); (G) (iv); (H) (x); (I) (vii); (J) (i)

- 8.5. (i) product, (ii) reactant, (iii) reactant

- 8.6. (i) open system, (ii) isolated system, (iii) isolated system.



$$8.8. \quad \begin{array}{l} \text{C}_{(\text{graphite})} \longrightarrow \text{C}_{(\text{diamond})} \quad \Delta H = 1.9 \text{ kJ} \\ 114 \text{ g octane on burning gave } 5200 \text{ kJ} \\ 1 \text{ kg would give heat} = \frac{5200}{114} \times 1000 = 45614 \text{ kJ} \end{array}$$

8.9. From the data

$$\Delta H_f \text{HCl}(\text{g}) = -92.3 \text{ kJ}$$

$$\Delta H_f \text{H}_2\text{O}(\text{l}) = -285.5 \text{ kJ}$$

$$(i) \quad \Delta H = [2x \Delta H_f \text{HCl}(\text{g}) + 2 \Delta H_f \text{H}_2\text{O}(\text{l})] - [4x \Delta H_f \text{HCl}(\text{g}) + \Delta H_f \text{O}_2(\text{g})]$$

Substituting the values

$$\Delta H = [2x0 + 2(-285.5)] - [4x(-92.3) + 0]$$

$$= -571 + 369.2 = -201.8 \text{ kJ}$$

$$(ii) \quad \Delta H = \frac{-201.8 \text{ kJ}}{4 \text{ mole HCl}} \times \frac{1 \text{ mole HCl}}{36.5 \text{ g}} = -1.38 \text{ kJ}$$

8.10. Increase. Higher kinetic energy increases disorder.

8.11. Increase in entropy

$$8.12. \quad \Delta G = \Delta H - T \Delta S$$

$$= 9600 - 378 \times 26 = -228 \text{ cal/mol}$$

$$8.13. \quad \Delta S = \Delta S(\text{g}) - \Delta S(\text{l}) = 298 - 205$$

$$= 93 \text{ J mol}^{-1} \text{ deg}^{-1}$$

$$T = \frac{\Delta H_{\text{vap}}}{\Delta S} = \frac{30.0 \times 10^3 \text{ J mol}^{-1}}{93 \text{ J mol}^{-1} \text{ deg}^{-1}} = 322.6 \text{ K}$$

$$= 49.6^\circ \text{C}$$

8.14. (i) ΔG is negative, thus the reaction is spontaneous

$$(ii) \quad \Delta S = \frac{\Delta H - \Delta G}{T}$$

$$= \frac{[-201.4 - (-192.5)] \times 10^3}{298} = -29.86 \text{ J/deg}$$

(iii) There is decrease in entropy, thus products are more ordered than the reactants.

Physical and Chemical Equilibrium

.... by equilibrium, we mean a state in which the properties of a system, as experimentally measured, would suffer no further observable changes even after the lapse of an indefinite period of time. It is not intimated that the individual particles are unchanging.

G.N. Lewis and M. Randall

UNIT PREVIEW

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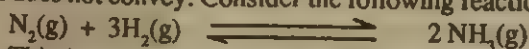
LEARNING OBJECTIVES

At the completion of this unit, you should be able to:

1. Distinguish reversible and irreversible physical and chemical changes
2. Differentiate between steady state and equilibrium state of a system
3. Identify the experiments to show physical equilibrium
4. Classify the phase equilibrium in different types
5. Characterize a state of equilibrium
6. Define law of chemical equilibrium
7. State the effect of concentration, temperature and pressure on the equilibrium
8. Define solubility of solid and gas in liquid
9. Calculate the equilibrium constants and equilibrium concentrations
10. Define and establish relationship between K_c and K_p
11. Define acids and bases
12. Describe the equilibrium when an electrolyte is dissolved in water
13. Discuss common ion effect
14. Describe ionic product of water, solubility product and p^H scale
15. Solve numerical problems on ionic equilibrium

9.1 INTRODUCTION

A balanced chemical equation gives a lot of quantitative information concerning the reactants and the products of a chemical reaction but there are many other important aspects of the reaction that it does not convey. Consider the following reaction,

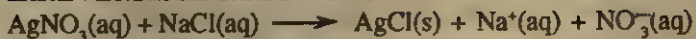


This is an important reaction in which combination of nitrogen and hydrogen gives ammonia—an industrially important product which is used in the manufacture of nitric acid and nitrogen fertilizers. The following questions, in this case, cannot be answered from the above balanced chemical equation:

1. To what extent does the reaction proceed in a given direction?
2. Do ammonia molecules decompose to give nitrogen and hydrogen back? If so what are the conditions that must be employed to prevent this back reaction?
3. What are the conditions that would give the maximum yield of ammonia?

These are few of the questions that can be answered from the study of chemical equilibrium, the topic of this unit. In this unit, we shall study different aspects of physical and chemical equilibrium by changing conditions of the reaction such as temperature, pressure and concentration(s) of either reactants or product(s).

9.2 IRREVERSIBLE REACTIONS



If we add 10 cm³ of 0.1M silver nitrate solution to 10 cm³ of 0.1M sodium chloride solution, a white precipitate is formed. Let us filter this solution. Now to the filtrate if more of silver nitrate solution is added, no more precipitate is formed and the reaction between AgNO₃ and NaCl may be considered complete. When stoichiometric quantities of the reactants are mixed, the reaction may go to completion and the course of reaction may not be affected by the addition of either the reactant or the product. Most ionic reactions are of this type in nature. Such reactions are called irreversible reactions. Thus, a reaction which proceeds to almost completion is called an irreversible reaction. An irreversible reaction is represented by writing a balanced equation for the reaction with an arrow (\longrightarrow) between the reactants and the products, heading towards the products of the reaction. Some irreversible reactions are :

- (i) heating potassium chlorate
- (ii) burning coal in air
- (iii) adding hydrochloric acid to sodium carbonate.

9.2.1 Characteristics of an Irreversible Reaction

- (i) under a given set of conditions, such a reaction proceeds only in one direction.
- (ii) most of these reactions are instantaneous
- (iii) at the end of the reaction the amount of the reactants left is almost negligible if these are mixed in stoichiometric ratio.

9.3 REVERSIBLE REACTIONS

9.3.1 Systems Involving Physical Changes

Here we shall consider systems which consist of one chemical species and changes in its physical state.

- (i) **Liquid changes to vapour and vice-versa**

Take water in a beaker and place a bell jar over it. If the level of

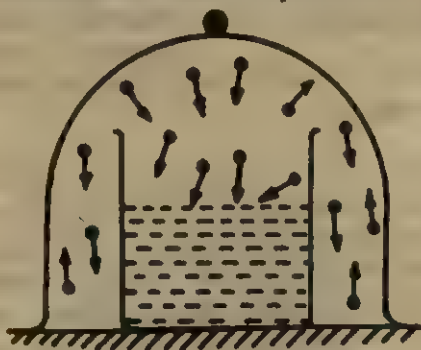


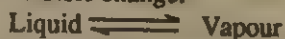
Fig.9.1 Evaporation of water in a closed vessel

water in the beaker is observed, it is found that initially the water level in the beaker drops but becomes constant after some time. Now the question arises why does water level in the beaker become constant ? It can be

answered as follows:

Water molecules leave the liquid phase and enter into vapour phase

until the pressure of the vapour in the bell jar attains a definite value (which is vapour pressure of water at the room temperature). The vapour phase water molecules are confined to a limited space. Inside the bell jar, there is every possibility that some of them condense and return back to the liquid phase. Thus, inside the bell jar water is changing to vapours and at the same time vapours are condensing to liquid. It is a reversible change.

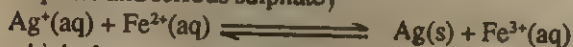


Exercise 9.1 : What would happen to water in a beaker if it is kept uncovered in air?

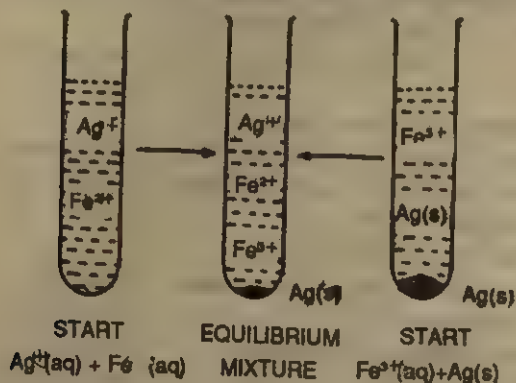
Solution : Water evaporates and the vapours are carried away in the atmosphere. Evaporation process continues till the entire water changes into the vapour form and escapes to the atmosphere.

9.3.2 Systems Involving Chemical Reactions

Consider the reaction between aqueous solutions of silver sulphate and ferrous sulphate,



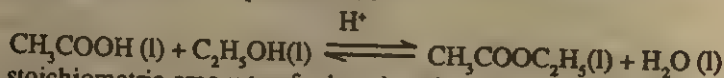
which does not proceed to completion. The reaction mixture has all the four species i.e., $\text{Fe}^{2+}(\text{aq})$, $\text{Fe}^{3+}(\text{aq})$, $\text{Ag}^+(\text{aq})$ and $\text{Ag}(\text{s})$. Such a situation is denoted by writing two half arrows (\rightleftharpoons) between the



reactants and the products of the reaction. A reaction which proceeds in either direction (Fig. 9.2), depending upon the conditions under which it is carried out, is called a reversible reaction.

Fig. 9.2 Example of a reversible reaction

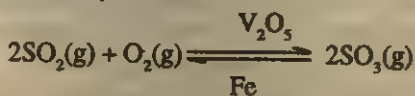
Consider the formation of ethylethanoate from ethanol and ethanoic acid in the presence of concentrated sulphuric acid. The reaction can be represented as



Take stoichiometric amounts of ethanoic acid and ethanol in different test tubes, add $1 \text{ cm}^3 4\text{N H}_2\text{SO}_4$, seal them and heat to 373K so that the reaction is complete. On analysing the contents of these test tubes, it was found that all the test tubes contained ethanol, ethanoic acid, ethylethanoate and water. This indicates that the reaction does not proceed to completion and it is a reversible reaction.

Some reversible reactions are :

1. Formation of hydrogen iodide : $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
2. Contact process

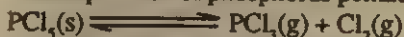


3. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \xrightleftharpoons[\text{Mo}]{\text{Fe}} 2\text{NH}_3(\text{g})$

4. Decomposition of dinitrogen tetraoxide



5. Decomposition of phosphorus pentachloride



9.3.3 Characteristics of Reversible Reactions

- (i) under the given conditions such a reaction proceeds in both the directions i.e., forward and reverse reactions go together.
- (ii) ordinarily it does not proceed to completion.

9.4 EQUILIBRIUM

9.4.1 Steady State

Examine a bunsen burner flame. There is a well defined structure of the flame—an inner cone surrounded by a luminous region of constant appearance. If the gas flow is adjusted so that it remains constant, the temperature of the flame at a particular spot does not change, yet the bunsen flame is not at equilibrium. Bunsen burner with a constant flow of gas where matter is passing continually into and out of it, is a steady state because it is an open system. Here some of its properties are constant but equilibrium does not exist.

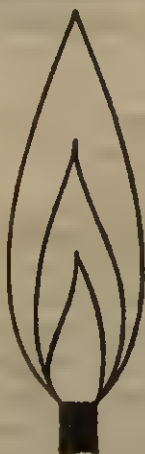


Fig. 9.3 Bunsen burner flame with hole open

9.4.2 Equilibrium State

- (i) **Phase equilibrium** : Figure 9.4 shows the addition of solid potassium permanganate to water. Initially the water is colourless (Fig. 9.4(a)) but soon a purple colour appears near the solid. Stirring the solution swirls of the violet colour to move out. Solid potassium permanganate is dissolving to become part of the solution (Fig. 9.4(b)). As the stirring is continued, the solution becomes deep violet and

the size of solid potassium permanganate particles diminishes. Finally, however, no visible change either in the colour of solution or the amount of solid potassium permanganate particles is observed (Fig. 9.4(c)). Since one cannot detect any change we say that the system has attained equilibrium. Equilibrium is characterized by constancy of macroscopic properties*.

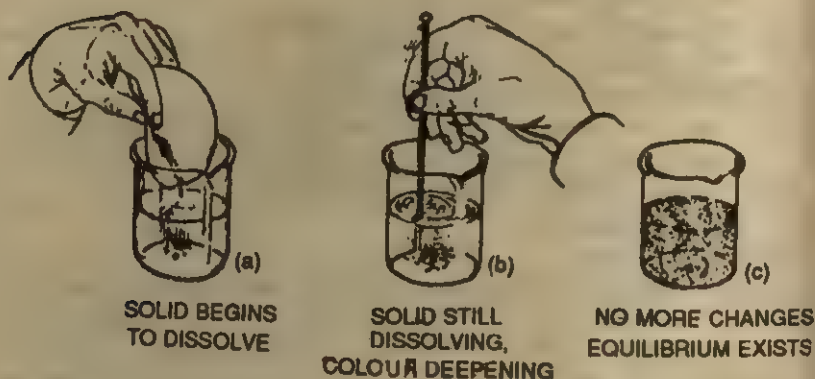


Fig. 9.4 Solid potassium permanganate dissolving in water

(ii) Chemical equilibrium

It has been seen (Section 9.3.2) that ethylethanoate can be formed from ethanol and ethanoic acid in the presence of H^+ ions. It can also be hydrolysed to ethanol and ethanoic acid under similar conditions. All reversible reactions have the common characteristic that their products can react to form the original reactants. The rate of the forward reaction decreases with time because the concentration(s) of the reactant(s) decrease. At the same time the concentrations of the products go on increasing and so the rate of the reverse reaction increases. The result is that at one stage the reactants are formed at the same rate at which they are being converted into the products. This is the state of equilibrium for the chemical reaction.

9.4.3 Characteristics of Equilibrium

- (i) equilibrium can exist only in a closed system**
- (ii) at equilibrium state, both the reactions, i.e., forward and reverse proceed, simultaneously. It is a dynamic state.

* Macroscopic means a large amount of material enough to see and weigh.

** A system containing a constant amount of the matter with all of this matter at the same temperature. A closed system can exchange energy but not matter with its surroundings.

- (iii) the rate of forward reaction is equal to the rate of reverse reaction.
- (iv) the state of equilibrium can be attained starting with either the reactants or the products.
- (v) at equilibrium the concentrations of the reactants and the products attain a constant value, called the equilibrium concentrations which do not change with the passage of time.
- (vi) at equilibrium, the change in free energy of the system, ΔG is zero at the given temperature and pressure.

Equilibrium is recognised by the constancy of macroscopic properties in a closed system at a uniform temperature

Exercise 9.2 : Which of the following systems exhibits steady state and which one is an example of equilibrium state ?

- (a) Water in a beaker is boiling on a burner. The temperature of the water is constant.
- (b) A balloon contains air and a few drops of alcohol. The pressure in the balloon is constant.

Solution :

- (a) Steady state because it is an open system.
- (b) Equilibrium state, balloon is a closed system and the equilibrium is, Alcohol (l) \rightleftharpoons Alcohol (g)

1. Evidence in favour of dynamic character of chemical equilibrium

An experimental evidence in favour of dynamic character of chemical equilibrium was provided by Wilson and Dickinson. For the reaction



Arsenous acid contained radioactive arsenic (atomic mass 76). At equilibrium, the concentration of each species is definite. They prepared a reaction mixture for the above reaction taking exactly the same amount of each specie as required at chemical equilibrium. They observed that after some time H_3AsO_4 also contained radioactive arsenic though the amount of H_3AsO_3 remained the same. It is possible only when some of $\text{As}^*\text{O}_3^{2-}$ changes to $\text{As}^*\text{O}_4^{3-}$ and the same amount of AsO_3^{3-} is being formed from AsO_4^{3-} .

2. Evidence to show that chemical equilibrium can be attained whether to start with reactants or products

Experiment 9.1 : Fill two identical bulbs marked A and B with dinitrogen tetroxide to equal pressure. Immerse the bulb A in ice at 273K and the bulb B in boiling water at 373K. Observe the colour in both the bulbs A and B.

Observation : Gas in bulb A is colourless.

Gas in bulb B is reddish brown.

Inference : As the colours in the two bulbs A and B are keeping them at different temperatures are different, the molecular species in these bulbs must also be different. Identification of the gases in these bulbs shows that the bulb A contains mostly dinitrogen tetroxide molecules. And bulb B contains only nitrogen dioxide.

Experiment 9.2 : Now transfer both the bulbs to a bath at room temperature as shown in Fig. 9.5 and note the colour change in both the bulbs A and B.

Observation : Colour changes in both the bulbs and finally attains the same intensity.

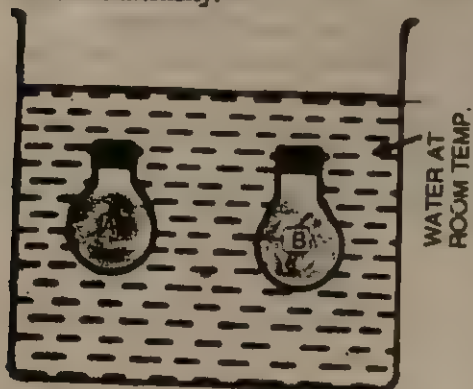


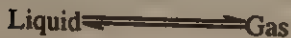
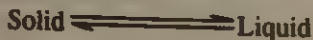
Fig. 9.5 Gases N_2O_4 and NO_2 when kept under similar conditions

In bulb A colour deepens to show that a chemical change is taking place forming NO_2 molecules from N_2O_4 . Bulb A:
 $N_2O_4(g) \longrightarrow 2NO_2(g)$.
 In bulb B colour fades to show again that a chemical change different from A is taking place. In this case now N_2O_4 is formed from NO_2 . Bulb B:
 $2NO_2(g) \longrightarrow N_2O_4(g)$

Inference : The above experiment confirms that the final state of a chemical reaction is the same irrespective of the starting material-reactants or products.

9.5 EQUILIBRIUM INVOLVING PHYSICAL CHANGES

An equilibrium system may consist of only one single substance distributed between two phases. Such equilibria are physical phase equilibria. Some important phase equilibria which are included in this unit are



9.5.1 Solid Liquid Equilibrium

Take 100 g each of water and ice at 273K and one atmosphere pressure in a perfectly insulated thermos flask (Fig. 9.6) so that there is no exchange of heat between its contents and the surroundings (adiabatic).

It will be observed that the shape of ice cube is different but the amounts of water and ice are the same. This observation may

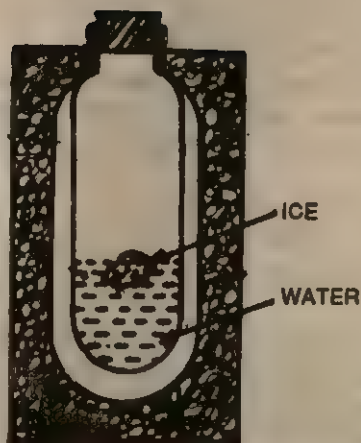
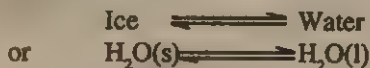


Fig. 9.6 Ice and water in a perfectly insulated thermos flask

be explained considering that some water molecules move towards ice and on reaching there adhere to it, at the same time some water molecules leave ice and mix with water. Thus, in a certain period of time water molecules which stick to ice are exactly the same as the number of water molecules that leave ice to mix with water. Here, an equilibrium between ice and water is established at 273K and 1 atm pressure.



9.5.2 Characteristics of Solid-Liquid Equilibrium

At equilibrium,

- (i) the masses of the two phases *i.e.* the solid phase and the liquid phase do not change.
- (ii) Both a solid and a liquid phase exert the same vapour pressure.
- (iii) $\Delta G = 0$ at the melting point of the solid and one atmosphere pressure.

If the system has temperature less than the melting point of solid, $\Delta G > 0$ and $\Delta G < 0$ at temperatures greater than the melting point (273K in case of ice-water equilibrium).

Exercise 9.3 : (i) 0.200 g iodine was stirred in 100 cm³ of water at 288K until equilibrium was reached. Calculate the masses of iodine in aqueous solution as well as undissolved (solid phase) if the concentration of iodine in aqueous solution at equilibrium was 0.0011 mol l⁻¹ at 288K.

(ii) What would be the concentrations of iodine in, aqueous solution and in solid phase if 150 cm³ of water was added to the equilibrium system from (i) and the system again attained equilibrium at 288K.

Solution: Molecular mass of I₂ = 254

At equilibrium :

Mass of I₂ in 1000 cm³ water = 0.0011 mol at 288K

Mass of I₂ in 1000 cm³ water = 0.0011 × 254g
= 0.2794g = 0.28g

Therefore, mass of I₂ in 100 cm³ water = $\frac{0.28 \times 100}{1000} = 0.028\text{g}$

- (ii) Mass of undissolved $I_2 = (0.200 - 0.028) = 0.172g$
 Addition of 150cm^3 more water would disturb the equilibrium, and more of I_2 would dissolve before the system attains equilibrium. Now the total volume of solution is $100 + 150 = 250\text{cm}^3$

$$\text{Mass of } I_2 \text{ in } 250\text{ cm}^3 \text{ solution} = \frac{0.28 \times 250}{1000} = 0.07g$$

$$\text{Undissolved iodine} = 0.200 - 0.070 = 0.130g$$

9.5.3 Liquid-Gas Equilibrium

When a liquid changes to vapour, the process is called vapourisation. This process can take place at all temperatures and in an open vessel, the process continues until entire liquid is evaporated. In evaporation, molecular movement is mainly in one direction. Molecules continuously leave the liquid and diffuse away into the air, it is an irreversible process (Fig. 9.7).

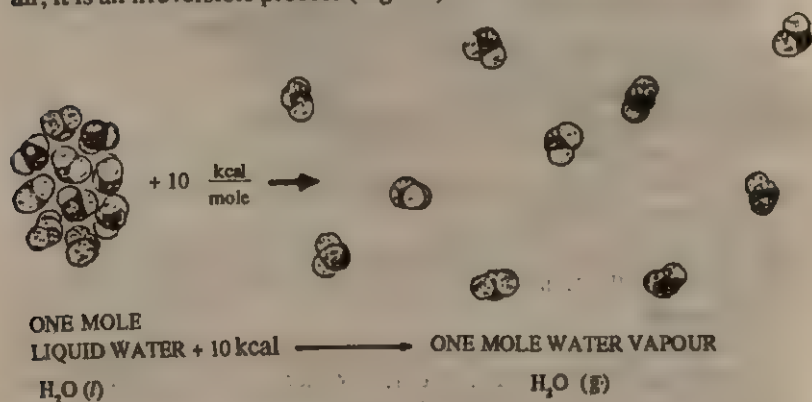


Fig. 9.7 Evaporation of water

Experiment 9.3 : Take a small amount of ethanol in four evacuated conical flasks marked A, B C and D. Place a bell-jar over these flasks and watch the liquid in these flasks (Fig. 9.8).

In these flasks initially the molecules move only in one direction i.e., from liquid to vapour but their rate of evaporation decreases with time, as shown in flasks A, B and C (Fig. 9.8). As time passes some of the ethanol molecules which are converted into vapours re-enter the liquid state and a stage comes when no change in the level of ethanol is observed (Fig. 9.8 ; flask D). This is the state when ethanol molecules leave the liquid form to change into vapour form with the same rate at which ethanol vapours condense to ethanol liquid. It is the state of equilibrium.

The equilibrium set up between a liquid and its saturated vapour can be expressed by the general equation.

Liquid \rightleftharpoons Vapour

ΔG for such a system at constant temperature is equal to zero.

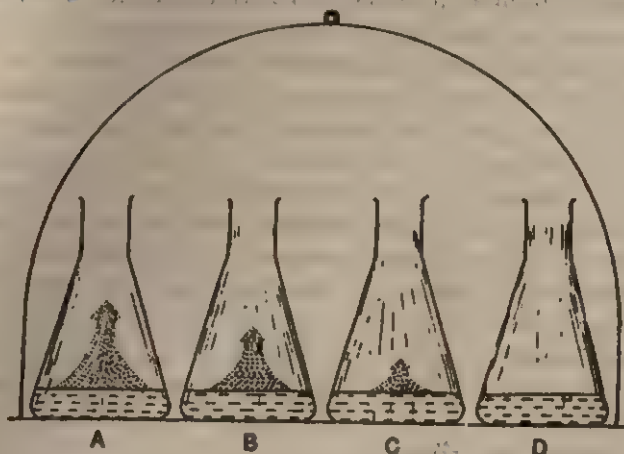


Fig. 9.8 Vaporisation of liquid when placed in evacuated flasks covered with a bell-jar.

Boiling Point - Vapour Pressure

Table 9.1 gives the normal boiling points and vapour pressures of some liquids.

TABLE 9.1 Vapour pressure and normal boiling point of liquids

Liquid	Vapour pressure at 293K (kPa)	Normal boiling point (K)
Acetone	12.36	333
Ethanol	5.85	351.5
Water	2.34	373.1

It can be seen from Table 9.1 that liquids which have a high value of vapour pressure boil at lower temperature compared to liquids which have low vapour pressure at the same temperature. In fact, a liquid boils when its vapour pressure becomes equal to the atmospheric pressure. Liquids which have high vapour pressure would need less heat. Thus, they have a lower value of molar heat of vapourisation and also a low boiling point.

Exercise 9.4 : A liquid is in equilibrium with its vapour in a sealed container at 340K. The volume of the container is suddenly increased.

(a) What is the immediate effect on the vapour pressure because of this sudden volume change?

(b) How do the rates of evaporation and condensation vary initially?

(c) When system attains equilibrium what will be the final pressure?

Solution : (a) Sudden increase in volume would initially decrease the initial vapour pressure of the liquid at the same temperature, (b) With sudden increase in volume of the container, the rate of evaporation increases because now the vapour pressure inside the container is less than that of the equilibrium vapour pressure. Since the container at this stage has less vapour than those needed to establish equilibrium, the rate of condensation would decrease. (c) Once the equilibrium is established the rate of evaporation would be equal to the rate of condensation. The final vapour pressure would be the equilibrium vapour pressure, i.e., the vapour pressure in the sealed container at the fixed temperature which is the same as it was before the increase in the volume of the container.

9.5.4 Solid-Gas Equilibrium

A solid can be in equilibrium with its vapour without involving the liquid state.



Ice can remain in equilibrium with its vapour, even when there is no liquid water present. Snow will evaporate slowly in dry air even when the temperature is quite low - below its freezing point.

Exercise 9.5: Why naphthalene balls in a clothes trunk disappear without forming a puddle ?

Solution : Naphthalene sublimates, i.e., changes directly to vapours and escapes.

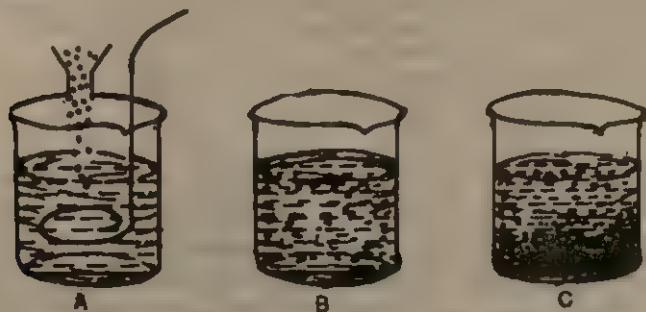


Fig. 9.9 Solid dissolving in a liquid.

9.5.5 Equilibrium Involving Dissolution of Solid in Liquid

When a solid is added to a liquid, solid starts dissolving in the liquid and its concentration increases. After all the solid has dissolved, the concentration remains constant at a particular

temperature. If we go on adding more and more solid to a definite volume of a liquid, a stage comes when no more solid dissolves *i.e.*, the addition of more solid no longer raises the concentration of dissolved material and now the added quantity remains in the solid state. A solution in contact with excess solid is said to be saturated at that temperature. In a saturated solution there exists a dynamic equilibrium between the solute molecules in solution and the solid solute particles.

Solid (dissolved) \rightleftharpoons Solid (undissolved)

If we consider sugar dissolved in water, the equilibrium can be expressed as Sugar (solid) \rightleftharpoons Sugar(aq)

The amount of solute dissolved in 100 g of a solvent to form a saturated solution at a given temperature, is termed as its solubility. Moreover, at the temperature, T , the vapour pressure of a solution containing a non-volatile solute such as sugar, sodium chloride *etc.*, is always less than the vapour pressure of pure solvent at the same temperature. Therefore, the boiling point of salt water is more than the boiling point of pure water. The increase in the boiling point of water, ΔT , depends upon the concentration of salt added to it. In a similar way, a lower temperature is required to crystallise ice from salt-water or from an ethanol water solution than from pure water. "ANTIFREEZE" substances added to an automobile radiator act on this principle.

9.5.6 Equilibrium Involving Dissolution of Gas in a Liquid

Gases also dissolve in liquids, *e.g.*, carbon dioxide dissolves in water (soda-water) and there exists an equilibrium between the gas dissolved in a liquid at a particular temperature and pressure.

Gas (in solvent) \rightleftharpoons Gas (in gaseous phase)

$\text{CO}_2(\text{aq}) \rightleftharpoons \text{CO}_2(\text{gas})$

The solubility of a gas in a liquid is expressed as **absorption coefficient** (α) introduced by Bunsen and is defined as, "The volume of the gas at STP, dissolved by unit volume of the solvent at the temperature of the experiment and under a pressure of 1 atm of the gas".

9.5.7 Factors Influencing the Solubility of a Gas in a Liquid

(i) **The nature of both gas and liquid** : A gas which chemically combines with a liquid is very soluble in that liquid, *e.g.*, ammonia in water.

(ii) **The temperature** : The solubility of a gas in a liquid decreases with increase in temperature. Dissolving a gas in a liquid usually evolves heat and ΔH for such processes is less than zero ($\Delta H < 0$).

(iii) **Effect of pressure upon solubility** : Pressure has a significant effect on gas solubility. At the given temperature, a rise in pressure increases the solubility of the gas. Increase in the pressure of the gas increases the concentration of solute molecules in the gas phase.

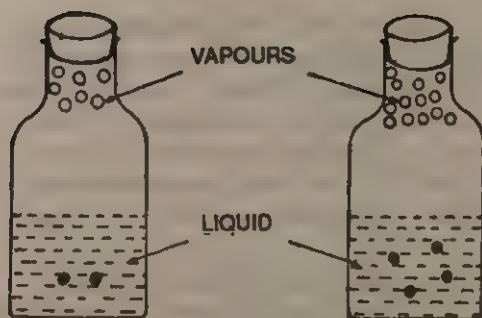


Fig.9.10 Effect of pressure on the solubility of a gas

To maintain equilibrium, the concentration of gas molecules in the liquid phase should also proportionately increase. The effect of pressure on the solubility of a gas at a given temperature is given by **Henry's law** which states "The mass of a gas dissolved in a given volume of a solvent at a particular temperature is proportional to the pressure of the gas above the solvent. If ' m ' is the mass of a gas dissolved in unit volume of solvent for a saturated solution and p is the gas pressure, according to Henry's law

$$\text{or } \frac{m}{p} = \text{constant}$$

Exercise 9.6 : When a bottle of soda water is opened, the carbon dioxide gas rapidly bubbles out of the bottle, explain.

Solution : Normally in soda water, carbon dioxide gas is filled at about 4 atm pressure. When the bottle is opened the pressure above the liquid drops to about 1 atm (atmospheric pressure) which reduces its solubility. Hence, it bubbles out rapidly.

9.5.8 General Characteristics of Physical Equilibrium

- (i) equilibrium can be attained only in a closed system, i.e., the system neither gains matter from the surroundings nor loses it to the surroundings. In other words there is no exchange of matter between the system and the surroundings.
- (ii) the equilibrium is dynamic but stable in nature. Equilibrium involves two opposite processes occurring simultaneously at the same rate. Thus, one process completely nullifies the effect of the other and there is no observable change.

(iii) one of the measurable properties such as temperature, pressure should remain constant since the composition of the system does not change.

(iv) when the system has attained equilibrium, there exists an expression involving concentration/partial pressure of the substances which reaches a constant value at a given temperature. The Table 9.2 lists the concentration related expressions for certain physical equilibria.

(v) the numerical value of the concentration - related expression is an indication of the extent to which the reaction proceeds before attaining the equilibrium.

TABLE 9.2 Different equilibria and constant in properties

Equilibrium	Constant property for a given condition
Solid \rightleftharpoons Liquid	Solubility of the solid in the given liquid at constant temperature.
Sugar(solid) \rightleftharpoons Sugar(aq)	Sugar(aq), i.e., concentration of sugar in its saturated solution which is its solubility at a given temperature.
Liquid \rightleftharpoons Gas	Vapour pressure at constant temperature
$H_2O(l) \rightleftharpoons H_2O(g)$	P_{H_2O} at a particular temperature
Liquid \rightleftharpoons Solid	Melting point of a solid at constant pressure.
$H_2O(l) \rightleftharpoons H_2O(s)$	Melting point of ice at constant pressure
Water \rightleftharpoons Ice	
Gas \rightleftharpoons Gas in liquid phase	Solubility of a gas in a liquid at constant temperature
$CO_2(g) \rightleftharpoons CO_2(aq)$	$[CO_2(aq)]$
	$\frac{[CO_2(aq)]}{[CO_2(g)]} = \text{Constant at a given temperature}$

9.6 EQUILIBRIUM INVOLVING CHEMICAL CHANGES

You have already seen Sections 9.3.2 and 9.3.3 that most of the chemical reactions do not proceed to completion, rather attain equilibrium just as is established in physical processes. In fact no reaction truly goes to completion. Sometimes, the concentration of the reactants left is very small or the rate of the reverse reaction is so low that it cannot be measured by the instruments available to us. Now the question arises, why do chemical reactions attain equilibrium?

Consider the reaction between hydrogen and iodine to form hydrogen iodide gas at 500K. Determine the concentrations of various species at different intervals of time and plot a graph concentration vs time (Fig. 9.11). It can be seen from the graph that, at the time of mixing, the rate of formation of HI is very large and H_2 and I_2 are also consumed quite fast. It follows that the concentrations of H_2 and I_2 will decrease with time whereas the concentration of HI

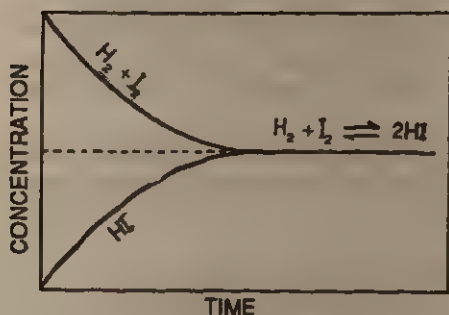


Fig. 9.11 Concentration change in a system vs time

will increase. Since the rate of reaction depends upon the concentrations of the reactants, we expect the rate of formation of HI to decrease with time. At the same time, as the concentration of HI is increasing, the rate of HI decomposition which initially was zero would increase.

Since the two

rates are in opposite direction, they must eventually become equal. When the rate of forward reaction is equal to the rate of reverse reaction the system is at the equilibrium state.

9.6.1 Altering the State of Equilibrium

Concentration/partial pressure and temperature are the two factors that affect the rates of reactions. Equilibrium is attained when the rate of reverse reaction is equal to the rate of forward reaction. Any condition that changes the rate of one of the reactions involved in the equilibrium may affect the conditions at equilibrium.

(i) **Concentration** : Consider the reaction between ferric ions and thiocyanate ions

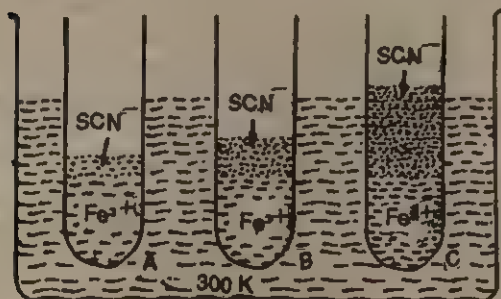
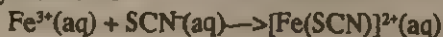


Fig. 9.12 Reactant concentrations affect the equilibrium state

Experiment 9.4 : Take 5cm^3 of ferric nitrate solution in three 15cm^3 test-tubes A, B and C (Fig. 9.12). Now to these test tubes, add 1, 2, 5cm^3 of 0.05M potassium thiocyanate solution. Observe the intensity of colour in these test tubes.

Observation : It is observed that the intensity of colour which is due to the formation of $[\text{Fe}(\text{SCN})]^{2+}(\text{aq})$ is maximum in the tube C, where the amount of SCN^- ions added is maximum, and is the minimum in the tube A, where the amount of SCN^- ions added is the least.

Inference : Equilibrium concentrations are affected if the concentrations of reactants (or products) are altered.

The concentration of $[\text{Fe}(\text{SCN})]^{2+}$ formed can be determined using the technique of colorimetry.

The initial concentrations of $\text{Fe}^{3+}(\text{aq})$ and $\text{SCN}^-(\text{aq})$ are known as in these test tubes, known volumes of standard solutions are taken. The equilibrium concentrations of these species can also be calculated by subtracting the amounts of $\text{Fe}^{3+}(\text{aq})$ and $\text{SCN}^-(\text{aq})$ reacted to form $[\text{Fe}(\text{SCN})]^{2+}$.

Substitute these equilibrium concentrations in the expression

$$\frac{[\text{Fe}(\text{SCN})]^{2+}}{[\text{Fe}^{3+}][\text{SCN}^-]} \quad \dots\dots (9.1)$$

which gives a constant value for the concentration ratio for all the three test tubes A, B and C provided temperature remains constant. It was attained in the above experiment by keeping these test tubes in a thermostat maintained at 300K . These results can be generalised in the form of a statement known as the "Law of Chemical Equilibrium".

9.6.2 Law of Chemical Equilibrium

(i) When equilibrium state is attained the rate of forward reaction, R_f , is equal to the rate of reverse reaction, R_r . Thus, at equilibrium,

$$R_f = R_r \quad \dots\dots (9.2)$$

According to the law of mass action*

$$R_f = k_f [\text{A}]^a [\text{B}]^b \quad \dots\dots (9.3)$$

$$R_r = k_r [\text{X}]^x [\text{Y}]^y \quad \dots\dots (9.4)$$

where k_f and k_r are the rate constants for the forward and reverse reactions respectively. The concentrations in equations 9.3 and 9.4 refer to the equilibrium concentrations. Substitute the value of R_f and R_r from equations 9.3 and 9.4 in equation 9.2.

$$k_f [\text{A}]^a [\text{B}]^b = k_r [\text{X}]^x [\text{Y}]^y \quad (\text{because } R_f = R_r) \quad \dots (9.5)$$

$$\text{or} \quad \frac{k_f}{k_r} = \frac{[\text{X}]^x [\text{Y}]^y}{[\text{A}]^a [\text{B}]^b} = K_c \quad \dots (9.6)$$

K_c is a constant, being called 'equilibrium constant' for a reaction.

* The use of square brackets in these equations 9.3 and 9.4 stands for concentrations of substances usually expressed in moles per litre. It will be used consistently.

It is independent of initial concentrations of the reactants or the products of the reaction but varies with temperature. The concentration ratio

$$\frac{[X]^a [Y]^b}{[A]^a [B]^b} \quad \dots \quad (9.6a)$$

is denoted by Q (concentration quotient) and $Q = K_c$ at equilibrium.

The equation 9.6 derived from the law of mass action, is a mathematical expression of the law of chemical equilibrium.

Irrespective of initial concentrations of the reactants and the products at equilibrium, the equilibrium concentrations are related to one another in such a way that the equation 9.6 is satisfied.

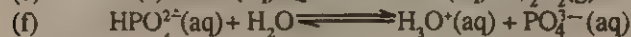
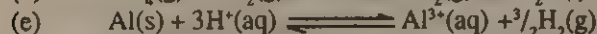
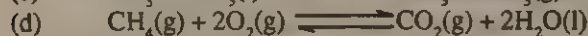
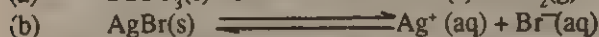
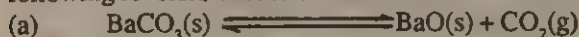
To write an expression for equilibrium constant

1. First write the balanced chemical equation for the reversible reaction.

2. For an expression for equilibrium constant, K_c , the numerator contains the algebraic product of the concentrations of the products, each raised to the power of its stoichiometric coefficient and the denominator contains the algebraic product of the concentrations of the reactants, each raised to the power of its stoichiometric coefficient, in the balanced chemical equation.

3. The molar concentrations of all solids is taken as 1.

Exercise 9.7: Write the equilibrium constant expressions for the following reversible reactions:



Solution :

(a) (i) Balanced chemical equation is

$$\text{BaCO}_3(\text{s}) \rightleftharpoons \text{BaO}(\text{s}) + \text{CO}_2(\text{g})$$

$$K_c = \frac{\text{BaO}(\text{s}) \times \text{CO}_2(\text{g})}{\text{BaCO}_3(\text{s})}$$

(ii) Substituting 1 for the concentrations of species which are in solid state at equilibrium in the above expression

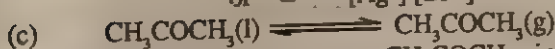
$$K_c = \frac{1 \times [\text{CO}_2(\text{g})]}{1} = [\text{CO}_2(\text{g})]$$

For reactions involving gases, it is more convenient to express concentration in terms of partial pressure, then we can write

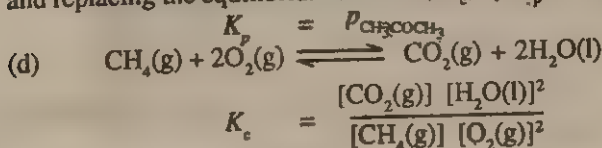
$$K_p = p_{\text{CO}_2}$$



$$K_c = \frac{[\text{Ag}^+(\text{aq})] [\text{Br}^-(\text{aq})]}{\text{or} = [\text{Ag}^+] [\text{Br}^-]}$$

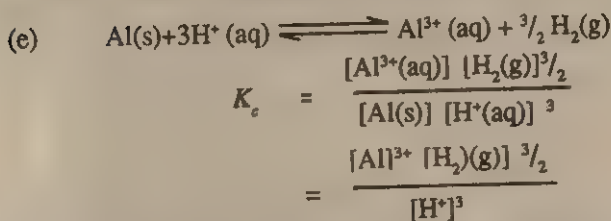


Concentration of acetone, CH_3COCH_3 , in the vapour form is proportional to its vapour pressure, i.e. $[\text{CH}_3\text{COCH}_3(\text{g})] \propto p_{\text{CH}_3\text{COCH}_3}$. In the liquid form when only one liquid is present, as in the above case, it is acetone, the concentration is taken as 1 (by convention) and replacing the equilibrium constant, K_c , by K_p , we have

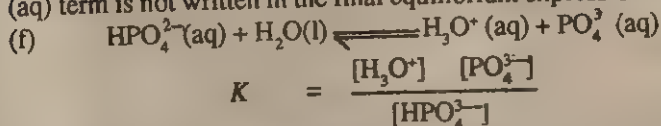


Substituting the concentrations of gaseous species by their respective partial pressures and concentration of liquid by 1 (by convention), we have

$$K_p = \frac{p_{\text{CO}_2}}{p_{\text{CH}_4} \times p_{\text{O}_2}^2}$$



(aq) term is not written in the final equilibrium expression.



In the study of chemical equilibrium, in solution, the concentrations are normally expressed in moles per litre and for equilibrium constant, K_c is commonly used. But in the study of equilibria in gaseous phase, it is more convenient to express concentrations in terms of partial pressures.

The expression for the partial pressure of an ideal gas, 'i' in a gaseous mixture is

$$p_i = x_i \times P \quad \dots (9.7)$$

p_i is the partial pressure for the gas i, x_i is its mole fraction, P is the total pressure of the gaseous mixture. At a constant pressure, P ,

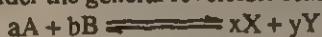
$$p_i \propto x_i \quad \dots (9.8)$$

partial pressure of an ideal gas is proportional to its mole fraction or to its molar concentration.

(ii) Expression for K_p

It is established that the partial pressure of a gas is proportional to its molar concentration (equation 9.8) so molar concentration in equation 9.6 can be substituted by partial pressures, then the symbol used for equilibrium constant is K_p .

Consider the general reversible reaction,



If at equilibrium, p_A , p_B , p_X and p_Y are the partial pressures of A, B, X and Y respectively. Then

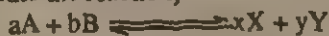
$$K_p = \frac{(p_X)^x (p_Y)^y}{(p_A)^a (p_B)^b} \quad \dots (9.9)$$

The pressures are to be expressed in atmosphere unless mentioned otherwise.

The numerical value of the equilibrium constant, K_c or K_p , depends only on the particular reaction and on the temperature.

9.6.3 K_p - K_c relationship

Consider the reaction,



$$K_p = \frac{(p_X)^x (p_Y)^y}{(p_A)^a (p_B)^b}$$

$$K_c = \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

For an ideal gas we know,

$$PV = nRT$$

where each symbol has usual meaning

$$\text{or } P = \frac{n}{V} RT$$

$\frac{n}{V}$ is number of moles per litre, i.e. molar concentration, C . Substituting C for $\frac{n}{V}$ in equation 9.13, we have,

$$P = CRT \quad \dots (9.10)$$

i.e. partial pressure = molar concentration \times gas constant \times temperature. Therefore, from equation 9.10

$$p_A = C_A \frac{RT}{V} \quad \dots\dots\dots (9.11)$$

$$p_B = C_B \frac{RT}{V} \quad \dots\dots\dots (9.12)$$

$$p_X = C_X \frac{RT}{V} \quad \dots\dots\dots (9.13)$$

$$p_Y = C_Y \frac{RT}{V} \quad \dots\dots\dots (9.14)$$

where C_A , C_B , C_X and C_Y are molar concentrations of A, B, X and Y respectively.

In the equation 9.9 substitute the values of partial pressures of A, B, X and Y in terms of their molar concentrations from equations 9.11 - 9.14.

$$K_p = \frac{(C_X RT)^x (C_Y RT)^y}{(C_A RT)^a (C_B RT)^b} \quad \dots\dots\dots (9.15)$$

$$= \frac{RT^{(x+y)} C_X^x \times C_Y^y}{RT^{(a+b)} C_A^a \times C_B^b} \quad \dots\dots\dots (9.16)$$

$$= \frac{(RT)^{(x+y) - (a+b)}}{C_A^a \times C_B^b} \quad \dots\dots\dots (9.17)$$

$$= (RT)^{\Delta n} K_c \quad \dots\dots\dots (9.18)$$

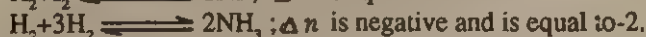
Where Δn is equal to $(x+y) - (a+b)$, i.e.,

$\Delta n = (\text{Number of moles of products}) - (\text{Number of moles of reactants})$

= Change in the number of moles in the reaction.

Δn is positive, zero or negative depending upon whether there is an increase, no change or decrease, respectively in the total number of moles in the reversible chemical reaction, e.g.,

For the reaction,



When Δn is equal to zero, i.e., there is no change in the total number of moles before and after a chemical reaction. In such cases,

$$K_p = K_c$$

9.6.4 Unit for Equilibrium Constant

(i) Unit for K_c

Consider the equation 9.6,

$$K_c = \frac{(\text{Moles/L of X})^x (\text{Moles/L of Y})^y}{(\text{Moles/L of A})^a (\text{Moles/L of B})^b}$$

$$= (\text{Moles per litre})^{(x+y) - (a+b)}$$

$$= (\text{Moles per litre})^{\Delta n}$$

K_c will have the dimension of

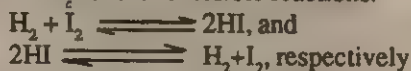
$$(\text{Moles per litre})^{\Delta n} \text{ or } (M)^{\Delta n}$$

Similarly K_p will have the dimension of
(Atmosphere) $^{\Delta n}$

When Δn is equal to zero, i.e., there is no change in the number of moles, K_p and K_c are just numerical values.

9.6.5 Factors affecting the Value of K

1. The mode of representing the equilibrium state : Calculate the value of K_c for the reversible reactions.



Let the equilibrium constant for the first and the second reactions be K_c and K'_c respectively.

It is customary to express k_f/k_r as K_c , therefore for the above reactions

$$\begin{aligned} K_c &= \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \\ K'_c &= \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} \\ K_c &= \frac{1}{K'_c} \quad \dots (9.19) \end{aligned}$$

Therefore, the mode of expressing a chemical equilibrium state influences the value of K . If an equation is reversed, the value of K_c is inverted.

2. Method of writing a balanced chemical equation : The reaction between nitrogen and ammonia can be represented as follows,



Equilibrium constant K_c , for this system is given by

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

The above reaction can also be written as -



Then the expression for the equilibrium constant, K_c would be

$$K_c = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}}$$

If the coefficients in a balanced chemical equation are multiplied by a common factor ($2, \frac{1}{2}, \dots$) the new equilibrium constant will be the old one raised to the corresponding power ($2, \frac{1}{2}, \dots$)

3. Change of temperature : Equilibrium constant changes with a change in temperature. Increase in temperature usually increases

the rate of a reaction, but the extent to which forward and reverse reactions are affected is different, hence, K is also different.

4. **Change in the units of expressing concentration :** For K_c , concentration is expressed in moles per litre and for K_p , partial pressure is expressed in atmosphere. If Δn is not equal to zero, any change in the units expressing concentrations or partial pressures of the constituents of reaction mixture will alter the numerical value of the equilibrium constant.

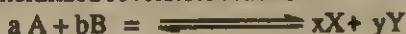
9.6.6 Factors which do not Influence the K Values

Following factors do not alter the value of equilibrium constant.

1. Initial concentrations of reactants or products
2. Addition of either of the constituents to the reaction mixture
3. Presence of a catalyst
4. Addition of an inert gas does not change the value of equilibrium constant
5. Time has no effect on the value of K .

9.6.7 Predicting the Direction of a Reaction

The numerical value of the equilibrium constant is determined experimentally. At any stage of the reaction the concentrations of the species involved in the reaction can be put in the expression (9.6a). For a generalized reversible reaction



the reaction quotient is

$$Q = \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

On substituting the concentrations of various species in the expression the value of reaction quotient Q is obtained. The numerical value of Q helps us in predicting the direction in which the reaction could take place.

(i) $Q = K_c$

When the concentrations of various species involved in the reaction are equilibrium concentrations in that case the value of Q is equal to K_c .

(ii) $Q < K_c$

When the calculated value of reaction quotient is less than the numerical value of K_c , then the reaction proceeds from left to right, i.e., forward reaction takes place until the equilibrium is established.

(iii) $Q > K_c$

When the value of reaction quotient is greater than that of the equilibrium constant K_c , in such a situation reaction proceeds to the left from the right until equilibrium is attained.

9.7 LE CHATELIER'S PRINCIPLE

We have seen earlier that the equilibrium remains unchanged

for an indefinite period unless some changes are made from outside, e.g., addition or removal of the reactants or the products (change of concentration), heating or cooling the system and change of pressure. The effect of these changes on chemical equilibrium can be predicted qualitatively in terms of 'Le Chatelier's principle'. It states, "When a system, in equilibrium, is subjected to a change in concentration, temperature or pressure, the equilibrium shifts in a way as to annul the effect of the change."

Accordingly :

(i) An increase of temperature will move the equilibrium in the direction in which the effect of added heat is minimized. Thus, an endothermic reversible reaction is favoured at high temperatures whereas an exothermic reaction will be favoured at low temperatures.

(ii) When a reversible reaction takes place with a change in volume, increase of pressure will try to shift the equilibrium in the direction which occurs with the decrease of volume.

(iii) For the effect of concentration on equilibrium, consider the reaction :



At equilibrium, definite concentrations of A, B, C and D are present. Now if we add more of A or B at this stage, more of C and D will be produced because in that way the added A or B is used up. Thus, according to Le Chatelier's principle the addition of A or B will produce larger concentrations of C and D at equilibrium.

The principle is equally applicable to both physical as well as chemical equilibria.

9.7.1 Application of Le Chatelier's Principle

(i) Physical Equilibrium (a) Melting of ice



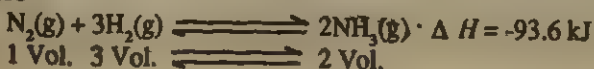
The melting of ice occurs with the absorption of heat and by a decrease in volume. Therefore, both the increase of pressure and temperature will cause more and more ice to melt.

(b) Vaporisation of water



When water is heated, it takes up heat and part of it is converted into vapour. Vaporisation of water is accompanied by a large increase in volume. According to the above principle, increase of pressure will cause the liquefaction-volume to decrease and increase of temperature will produce more vapours (to cause more and more absorption of heat).

(ii) Chemical Equilibrium (a) Formation of ammonia by Haber's process

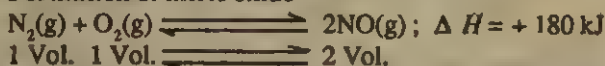


Since this reaction is exothermic, i.e., heat is evolved when the forward reaction takes place, a low temperature will favour the forward reaction. Thus, if the temperature is raised, equilibrium concentration of ammonia will decrease and those of N_2 and H_2 will increase.

One volume of N_2 and 3 volumes of H_2 combine to form 2 volumes of ammonia, the reaction proceeds in the forward direction with the decrease of volume. Therefore, high pressure will favour the formation of ammonia.

According to Le Chatelier's principle, the increase of any component of the reaction mixture will shift the equilibrium in the direction in which the added components are used up. Addition of N_2 or H_2 will result in higher yield of ammonia.

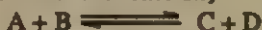
(b) **Formation of nitric oxide**



The forward reaction is endothermic and there is no volume change during the reaction. In this case, we conclude that (i) increase of temperature will favour the formation of NO. (ii) the equilibrium will remain unaffected by change in pressure, and (iii) the formation of NO will be favoured by an excess of N_2 or O_2 .

9.7.2 Effect of Catalyst on Equilibrium

Consider the reaction,



When the reaction has attained equilibrium the change in free energy, ΔG , is equal to zero at constant temperature and pressure. That is the sum of the free energies of the reagents on the LHS of the equation is equal to the sum of the free energies of the reagents on the RHS of the chemical equation. A catalyst does not take part in the chemical reaction, as such it does not figure in the chemical equation and for that reason in the expression for chemical equilibrium constant, K_c . Thus, we can say a catalyst does not affect the value of equilibrium constant. However, a catalyst increases the rate of forward as well as reverse reactions and thereby it will help the equilibrium to establish quickly.

9.8 APPLICATION OF LAW OF CHEMICAL EQUILIBRIUM

By application of the law, the equilibrium constant of the reaction and the equilibrium concentrations can be calculated. The examples given below illustrate the procedure.

Exercise 9.8 : 35.7 g of PCl_5 were taken in a 5 litre flask and heated in a thermostat at 523K until the following equilibrium was established



It was found that at equilibrium 8.75g of Cl_2 was present. Calculate the equilibrium constant for the above reaction.

Solution : Initial concentration of PCl_5 in mol L^{-1} = $\frac{35.7 \times 1}{208 \times 5}$
 = 0.0343

Concentration of Cl_2 in mol L^{-1} at equilibrium
 = $\frac{8.75}{71} \times \frac{1}{5} = 0.0246$

Since the concentrations of Cl_2 and PCl_3 should be equal at equilibrium, therefore, equilibrium concentration of PCl_3 is also 0.0246 mol L^{-1} . This also means that 0.0246 mol L^{-1} of PCl_5 is dissociated at equilibrium. Thus, equilibrium concentration of PCl_5 = (Initial conc. — Amount dissociated) = 0.0343 — 0.0246 = 0.0097 mol L^{-1} .

Now, $K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{0.0246 \times 0.0246}{0.0097} = 6.2 \times 10^{-2} \text{ mol L}^{-1}$

Exercise 9.9 : What will be the equilibrium concentrations of each species present when 2 moles of HI are introduced in a litre vessel at 763K? The value of K_c for the reaction $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ is 0.022 at 763K. What fraction of HI decomposes ?

Solution : Let us suppose that $2x$ moles of HI are dissociated at equilibrium. Then, from the above equation, x moles H_2 and x moles of I_2 will be produced. The initial and equilibrium concentrations of HI, I_2 and H_2 can thus be written as :

	[HI]	[H ₂]	[I ₂]
Initial concentration (mol L^{-1})	2	0	0
Equilibrium concentration (mol L^{-1})	(2-2x)	x	x

Thus, $K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{x \cdot x}{(2-2x)^2} = 0.022$

or $x = 0.229$. Thus, molar concentrations at equilibrium are :

$\text{HI} = 2 - (2 \times 0.229) = 1.542 \text{ mol L}^{-1}$

$\text{H}_2 = \text{I}_2 = 0.229 \text{ mol L}^{-1}$

The fraction of HI decomposed = $\frac{(2-1.542)}{2} \times 100 = 22.9\%$

9.8.1 Heterogeneous Equilibrium

The law of chemical equilibrium may also be applied to the study of equilibrium in which the reacting species are not in the same phase (heterogeneous equilibrium). For the reaction, $\text{Zn}(\text{s}) + \text{CuSO}_4(\text{aq}) \rightleftharpoons \text{ZnSO}_4(\text{aq}) + \text{Cu}(\text{s})$ on applying the law of mass action the equilibrium constant is given by

$K_c = \frac{[\text{ZnSO}_4(\text{aq})][\text{Cu}(\text{s})]}{[\text{Zn}(\text{s})][\text{CuSO}_4(\text{aq})]}$

By taking Cu (s) and Zn (aq) equal to zero the expression becomes,

$$K_c = \frac{[\text{ZnSO}_4]}{[\text{CuSO}_4]} \quad \dots (9.20)$$

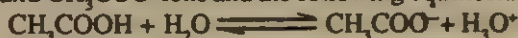
9.9 IONIC EQUILIBRIUM

In 1887, Arrhenius for the first time explained that when an electrolyte (a substance which conducts electricity in solution) is dissolved in a solvent, a portion or all of it dissociates into ions. The amount of an electrolyte present as ions varies with (i) its concentration, (ii) solvent used, (iii) presence of other electrolytes and (iv) temperature. Electrolytes like HCl, H_2SO_4 , NaOH, etc. are almost completely dissociated into ions in aqueous solutions. For example, all the HCl will be present as H^+ (more correctly H_3O^+ , hydronium) ions and Cl^- ions in water. These are called strong electrolytes. On the other hand, electrolytes such as CH_3COOH , NH_4OH , etc. do not dissociate completely in solution. For example, when acetic acid is dissolved in water, H_3O^+ and CH_3COO^- ions and undissociated CH_3COOH molecules are present. Such substances are referred to as weak electrolytes.

In the case of electrolytes, an equilibrium exists between the unionized molecules and the ionic species. The principle used in describing ionic equilibria is the same as that of chemical equilibrium

9.9.1 Ionization of Weak Electrolytes

When acetic acid is dissolved in water, it dissociates partly into H_3O^+ and CH_3COO^- ions and the following equilibrium is established



Applying the law of mass action

$$K_c = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]}$$

In a dilute solution, H_2O can be taken as constant. The product of K_c and H_2O is denoted as K_a , the ionization or dissociation constant of the acid.

$$\text{Thus } K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} \quad \dots (9.21)$$

If C represents the original concentration of the acid in mol L^{-1} and α is the degree of dissociation, then the equilibrium concentration of each of the ions (CH_3COO^- and H_3O^+) will be $C\alpha$

$$\text{Therefore, } K_a = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \quad \dots (9.22)$$

In case of weak electrolytes when the value of α is very small, $(1-\alpha) \approx 1$. Now the expression becomes,

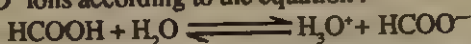
$$K_a = C\alpha^2 \text{ or } \alpha = \sqrt{\frac{K_a}{C}} \quad \dots (9.25)$$

The degree of dissociation, α , can therefore be calculated at a given concentration C , if K_a is known. Since C is reciprocal of V (V is the volume in litres containing moles of an electrolyte) we have,

$$\alpha = \sqrt{K_a V} \quad (9.23)$$

Exercise 9.10 : Calculate the degree of dissociation and the concentration of H_3O^+ ions of 0.01 M solution of formic acid. $K_a = 2.1 \times 10^{-4}$ at 298K.

Solution : Formic acid is a weak electrolyte and ionises in water to give H_3O^+ ions according to the equation :



Let α be the degree of dissociation. Then, the concentration of the various species present at equilibrium would be as under :

$$[\text{H}_3\text{O}^+] = C\alpha = 0.01\alpha; [\text{HCOO}^-] = C\alpha = 0.01\alpha; [\text{HCOOH}] = C(1-\alpha) = 0.01.$$

Now using the equation (9.22),

$$K_a = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{0.01 \times 0.01 \times \alpha^2}{0.01} = 0.01\alpha^2 = 2.1 \times 10^{-4}$$

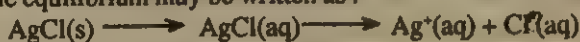
$$\alpha^2 = \frac{2.1 \times 10^{-4}}{0.01} = 2.1 \times 10^{-2}$$

$$\text{Degree of dissociation, } \alpha = \sqrt{2.1 \times 10^{-2}} = 0.14$$

$$\text{Concentration of } \text{H}_3\text{O}^+ \text{ ions} = C\alpha = 0.01 \times 0.14 = 1.4 \times 10^{-3} \text{ mol L}^{-1}$$

9.10 SOLUBILITY PRODUCT

Insoluble substances like AgCl , BaSO_4 , PbCl_2 , are in fact not completely insoluble when present in aqueous medium. A very small amount of these dissolve and is present as ions. Further there exists an equilibrium between the undissolved and the dissolved salt. For AgCl , the equilibrium may be written as :



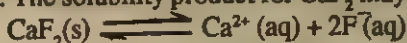
Applying the law of chemical equilibrium.

$$K = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

$[\text{AgCl}]$ may be taken constant because of the fact that very little of this solid dissolves in aqueous solution (by definition).

$$\text{Thus, } K \times [\text{AgCl}] = K_{sp} = [\text{Ag}^+][\text{Cl}^-] \quad \text{.....(9.24)}$$

The constant K_{sp} is known as solubility product, and $[\text{Ag}^+][\text{Cl}^-]$ as ionic product. The ionic product is equal to the solubility product, K_{sp} , in a saturated solution of a sparingly soluble electrolyte. For a salt M_mX_n , dissolved in water, $K_{sp} = [\text{M}^{n+}]^m [\text{X}^{m-}]^n$ where M^{n+} and X^{m-} are molar concentrations of ionic species M^{n+} and X^{m-} in a saturated solution. The solubility product for CaF_2 may be written as :



$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2$$

The different sparingly soluble substances are characterized by definite values of solubility product at a given temperature (Table 9.3). The value of the solubility product can be calculated from the

knowledge of the solubility of the sparingly soluble substance at a given temperature.

TABLE 9.3. Solubility products (K_{sp}) of some sparingly soluble salts at 298K

Salt	K_{sp}	Salt	K_{sp}
AgCl	1.7×10^{-10}	CuS	8.0×10^{-37}
AgBr	5.0×10^{-13}	ZnS	7.0×10^{-26}
AgI	8.5×10^{-17}	HgS	1.6×10^{-52}
PbCl ₂	1.7×10^{-8}	CdS	1.4×10^{-28}

Exercise 9.11 : At 298K, 0.00188g of AgCl dissolves in one litre of water. What is the K_{sp} for AgCl?

Solution : $[Ag^+] = \frac{0.00188}{143.5} = 1.31 \times 10^{-5} \text{ mol L}^{-1}$

Now, $[Ag^+] = [Cl^-]$

Therefore, $K_{sp} = [Ag^+] [Cl^-] = 1.31 \times 10^{-5} \times 1.31 \times 10^{-5}$
 $= 1.7 \times 10^{-10}$

Exercise 9.12 : If K_{sp} for CaF_2 is 1.7×10^{-10} at 298K, calculate its solubility in mol L^{-1}

Solution : CaF_2 ionizes in solution as : $CaF_2(s) \rightleftharpoons Ca^{2+} + 2F^-$.

In this case, for each mole of Ca^{2+} , twice the moles of F^- ions will be present at equilibrium. Let x be the solubility of CaF_2 . Then, x moles of Ca^{2+} and $2x$ moles of F^- are present in a saturated solution of CaF_2 .

$$K_{sp} = 1.7 \times 10^{-10} = [Ca^{2+}] [F^-]^2 = x \times (2x)^2 = 4x^3$$

or $x = 3.5 \times 10^{-4}$

Therefore, solubility of $CaF_2 = 3.5 \times 10^{-4} \text{ mol L}^{-1}$

9.11 COMMON ION EFFECT

Consider the dissociation of a weak acid, e.g., HCN



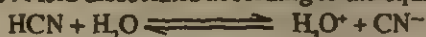
$$K_a = \frac{[H_3O^+] [CN^-]}{[HCN]}$$

It means that K_a has a constant value at a given temperature. If HCl is added to the above equilibrium, then, the concentration of H_3O^+ is greatly increased. In order that K_a remains constant, the value of CN^- should decrease and that of undissociated HCN should increase. In other words, the above equilibrium will shift towards the left, thereby reducing the dissociation of HCN. In a similar manner, the ionization of HCN is suppressed in the presence of NaCN which furnishes an excess of CN^- ions. Thus, the dissociation of HCN is suppressed in the presence of both H^+ and CN^- ions. It implies that the dissociation of a weak acid is suppressed by the addition of a substance capable of furnishing an excess of ions common to either of the ions of the acid. Arguing in a similar manner, it can

be concluded that the dissociation of a weak base, *e.g.*, NH_4OH will be suppressed by the addition of either NH_4Cl or NaOH . This effect is called the **common ion effect**. It may be summarized as; "The dissociation of a weak electrolyte is suppressed (reduced) on addition of a strong electrolyte having an ion common with that of the weak electrolyte".

Exercise 9.13 : A weak acid, HCN , is dissolved in water so that the initial concentration is 0.1 mol L^{-1} . It is found to be 1% dissociated. What is the dissociation constant? Calculate the concentration of H_3O^+ ions when KCN having the concentration 1.0 mol L^{-1} is added to it.

Solution : Acid dissociates according to the equation



It is only 1% acid that dissociates. Therefore, the concentration of HCN dissociated = $[\text{HCN}] [0.01]$

$$= (0.1)(0.01) = 0.001 \text{ mol/L}$$

$$[\text{H}_3\text{O}^+] = 0.001 \text{ mol/L}; [\text{CN}^-] = 0.001 \text{ mol/L}$$

$$\text{HCN}_{(\text{undissociated})} = 0.1 - 0.001 = 0.1$$

Dissociation constant, K_a

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{0.001 \times 0.001}{0.1} = 1.0 \times 10^{-5}$$

After adding KCN : Let the concentration of H_3O^+ be $x \text{ mol/L}$

$$[\text{CN}^-]_{\text{total}} = [\text{CN}^-]_{\text{KCN}} + [\text{CN}^-]_{\text{(from dissociation of HCN)}}$$

$$[\text{CN}^-]_{\text{KCN}} = 1.0 \text{ mol/L} \quad (\text{since } \text{CN}^- \text{ from the dissociated HCN is very small})$$

$$[\text{HCN}] = 0.1 \quad \text{H}_3\text{O}^+ \approx 0.1 \quad (\text{due to small ionization of HCN})$$

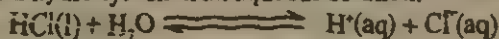
$$K_a = \frac{[\text{H}_3\text{O}^+] \times 1.0}{0.1} = 1.0 \times 10^{-5}$$

$$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-6} \text{ mol/L}$$

9.12 ACID BASE EQUILIBRIUM

9.12.1 Acid-Base Concepts

(i) Arrhenius (1887) defined an acid as a substance that will dissociate to yield hydrogen ion while a base is one that will dissociate to yield hydroxyl ion in an aqueous solution.

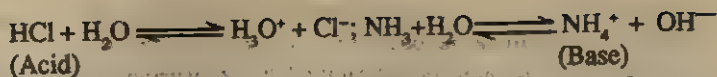


(Acid)



(Base)

(ii) The Arrhenius concept excluded several substances which were either acids or bases. Lowry and Bronsted (1923) observed that an acid reacted with water in a manner opposite to that of a base. For example, HCl (an acid) donates a proton to water molecule while NH_3 (a base) accepts a proton from water molecule, *i.e.*,



On this basis they postulated that “species having a tendency to donate a proton are acids and those which accept a proton are bases”. Thus, in the first reaction above, HCl is an acid and water is a base. In the other reaction H₂O is an acid and NH₃ is a base; NH₄⁺ is an acid and OH⁻ is a base. Hence, we are led to the conclusion that for an acid-base equilibrium, there are two acid-base pairs. The base formed from an acid is referred to as the conjugate base of the acid. Correspondingly, the acid formed from a base is called the conjugate acid of the base. An acid-base pair differing by a proton constitutes a conjugate acid-base pair. For the above reaction, Cl⁻ is the conjugate base of HCl and H₂O is the conjugate base of H₃O⁺; HCl is the conjugate acid of base Cl⁻ and H₃O⁺ is the conjugate acid of base H₂O. This concept is further illustrated below (Table 9.4) for a series of common acids and bases

TABLE 9.4 - Conjugate acid-base pairs

Acid ₁		Base		Acid ₂		Base ₂
HNO ₃	+	H ₂ O	→	H ₃ O ⁺	+	NO ₃ ⁻
NH ₄ ⁺	+	H ₂ O	→	H ₃ O ⁺	+	NH ₃
H ₂ O	+	CN ⁻	→	HCN	+	OH ⁻
H ₂ O	+	NH ₃	→	NH ₄ ⁺	+	OH ⁻
HCl	+	NH ₃	→	NH ₄ ⁺	+	Cl ⁻
H ₂ SO ₄	+	H ₂ O	→	H ₃ O ⁺	+	HSO ₄ ⁻
H ₂ O	+	CO ₃ ²⁻	→	HCO ₃ ⁻	+	OH ⁻
HCN	+	H ₂ O	→	H ₃ O ⁺	+	CN ⁻

Strengths of Acids and Bases

Since acids are substances capable of losing a proton, the tendency to lose a proton would be a measure of its acid strength. Similarly, the strength of a base is determined by its tendency to accept a proton. In this respect, a strong acid would have least affinity for a proton and get completely dissociated to give a proton. This means that its conjugate base cannot hold the proton and is thus a weak base. For example, in an aqueous solution, HCl is a strong acid and its conjugate base, Cl⁻ is a weak base. In general, the stronger the acid, the weaker is its conjugate base. Conversely, the conjugate base of a weak acid is a strong base, *e.g.*, CN⁻ is a strong conjugate base of the weak acid, HCN.

A strong base, on the other hand, has a strong affinity for a proton. Therefore, the conjugate acid of a strong base is a weak acid and the conjugate acid of a weak base is a strong acid. The stronger the base, the weaker is its conjugate acid. In water, CO₃²⁻ is a strong

base and HCO_3^- is its weak conjugate acid. Similarly, NH_4^+ is a strong conjugate acid of the weak base, NH_3 .

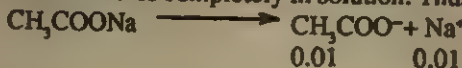
The strength of an acid is determined by measuring its dissociation constant, K_a . The larger the K_a , the stronger is the acid. For example, K_a for HF is 6.7×10^{-4} while that of acetic acid is 1.8×10^{-5} . It means that the dissociation of HF in water is more as compared to that of CH_3COOH . Thus, the former is a stronger acid.

Exercise 9.14 : Find the concentration of H_3O^+ ions in a mixture of 0.002 M CH_3COOH and 0.01 M CH_3COONa . The dissociation constant for acetic acid is 1.8×10^{-5} .

Solution : Acetic is a weak acid and ionizes partly. Let x be its degree of ionization. We have :



Sodium acetate ionizes completely in solution. Thus :



In Solution :

$$\begin{aligned} [\text{CH}_3\text{COO}^-]_{\text{total}} &= [\text{CH}_3\text{COO}^-] (\text{from acid}) + [\text{CH}_3\text{COO}^-] (\text{from salt}) \\ &= 0.002x + 0.01 \\ &= 0.01 \text{ (as } x \text{ is very small)} \end{aligned}$$

$$[\text{CH}_3\text{COOH}] = 0.002(1-x) = 0.002 \text{ (as } x \text{ is very small)}$$

Substituting the values in the expression for K_a , we have

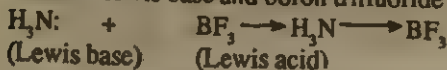
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \text{ or } 1.8 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+] \times 0.01}{0.002}$$

$$\text{Thus, } [\text{H}_3\text{O}^+] = \frac{1.8 \times 10^{-5} \times 0.002}{0.01} = 3.6 \times 10^{-6} \text{ mol L}^{-1}$$

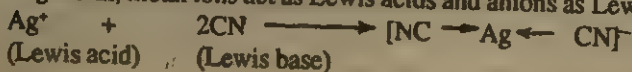
(iii) Lewis (1923) defined substances as acids and bases in terms of electrons pair. When an acid donates a proton to a water molecule, it may also be seen that proton accepts an electron pair from the oxygen atom of H_2O .



According to Lewis : The species which are capable of accepting a pair of electrons are acids and those which can donate a pair of electrons are bases". In the following reaction between NH_3 and BF_3 , nitrogen donates an electron pair to boron. Thus, ammonia is called a Lewis base and boron trifluoride a Lewis acid.



In general, metal ions act as Lewis acids and anions as Lewis bases





(Lewis acid) (Lewis base)

9.12.2 Ionization of Water

In the ionic reactions, water is used as solvent. Water can act as an acid as well as a base which depends on the substances with which it reacts. The ionization of water can be represented as



Thus, even if we do not add an acid or a base in water, some H_3O^+ and OH^- ions will always be present in it. The equilibrium constant for the ionization of water can be written as,

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

As water is a weak electrolyte, $[\text{H}_2\text{O}]$ can be taken constant. The product of $K \times [\text{H}_2\text{O}]$ is known as ionic product of water (K_w).

$$\text{Hence, } K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad \dots (9.25)$$

At 298K, we know that

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7}$$

$$\text{Hence } K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$$

As the dissociation of water varies with temperature, the K_w of water is different at different temperatures. For example at 323K,

$$K_w = 5.48 \times 10^{-14}$$

9.12.3 Effect of addition of an Acid or a Base on Ionization of Water

Addition of an acid or a base would bring a change to the extent water ionizes i.e. the H_3O^+ and OH^- will increase or decrease. Addition of an acid increases the H_3O^+ ions concentration in water while addition of a base decreases $[\text{H}_3\text{O}^+]$. However, the ionic product of water will remain constant at a given temperature.

Exercise 9.15 : The OH^- concentration of an aqueous solution is $10^{-6} \text{ mol L}^{-1}$ at 298K. Find out the concentration of H_3O^+ ions.

Solution : We know $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

$$\text{or } \text{H}_3\text{O}^+ = \frac{K_w}{[\text{OH}^-]}$$

$$= \frac{10^{-14}}{10^{-6}} = 10^{-8} \text{ mol L}^{-1}$$

Exercise 9.16 : The $[\text{H}_3\text{O}^+]$ in a solution is $5.48 \times 10^{-6} \text{ mol L}^{-1}$ at 323K. Find $[\text{OH}^-]$. Given K_w at 323K = $5.48 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$

Solution : We know $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

$$\text{or } [\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{5.48 \times 10^{-14}}{5.48 \times 10^{-6}} = 10^{-8} \text{ mol L}^{-1}$$

9.12.4 pH Scale

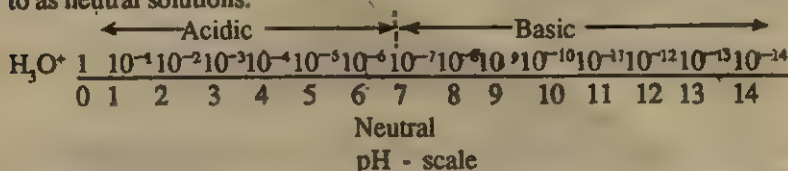
The addition of an acid or a base brings a change in $[H_3O^+]$ ions in water solutions. A 1M solution of a strong acid contains 1 mol L^{-1} H_3O^+ ions. Thus, the concentration of H_3O^+ ions in water may change from 1 or more moles per litre to 10^{-4} or less. Also, H_3O^+ concentration affects a large number of biological and industrial processes; its use in the studies is important to ascertain the acid-base behaviour of a solution. Sorenson (1909) suggested a new scale to express the concentration of H_3O^+ ions in an aqueous solution which is known as pH scale. He defined pH as the negative logarithm (base 10) of H_3O^+ concentration in moles per litre.

$$pH = -\log_{10} [H_3O^+] \quad \dots (9.26)$$

Thus, at 298K, pH of water is

$$pH = -\log [10^{-7}] = 7$$

when an acid is added to water, H_3O^+ concentration increases and consequently pH of the solution will always be less than 7. Similarly, addition of a base to the solution will result a pH higher than 7. Thus, one can say that an acidic solution will have pH less than 7 and a basic solution more than 7. Solutions of pH = 7 are referred to as neutral solutions.



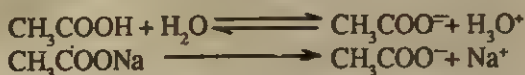
Exercise 9 17 : What is the pH of a solution whose H_3O^+ ions concentration is $5.2 \times 10^{-8} \text{ mol } L^{-1}$.

$$\begin{aligned} \text{Solution : } pH &= -\log 5.2 \times 10^{-8} \\ &= -[\log 5.2 + \log 10^{-8}] \\ &= -0.716 + 8 \\ &= 7.284 \end{aligned}$$

9.12.5 Buffer Solution

The solutions which resist pH change when small amounts of acids or bases are added to them are called 'buffer solutions'. They contain a weak base and its salt with a strong acid (e.g., $NH_4OH + NH_4Cl$)

Let us see how such a solution works, taking an example of CH_3COOH and CH_3COONa buffer. The species present in solution are :



The ionization of acetic acid is very small due to the presence of an excess of its common ion, i.e., acetate ions. Thus, the buffer solution contains a large amount of unionized acetic acid, large amount of

acetate ions and a small amount of H_3O^+ ions. If a strong acid like HCl is added to this solution, H^+ ions from HCl will combine with the acetate ions present in the solution to form unionized acetic acid. Hence, H_3O^+ ion concentration, or pH of the solution remains essentially the same as that of the original solution. On the other hand, when a strong base like NaOH is added to the buffer solution; OH^- ions from NaOH react with H_3O^+ ions present in the solution to form unionized water. The decrease in the concentration of H_3O^+ ions is made up by the tendency of the acetic acid equilibrium ($\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$) to get readjusted. Arguing in the same manner, it can be concluded that a mixed solution of NH_4Cl and NH_4OH will resist any change in its pH value on the addition of a small amount of an acid or a base.

9.12.6 pH of Buffers

To determine the pH of an acid buffer (a weak acid + its salt), the following equation is used

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad \dots \quad (9.27)$$

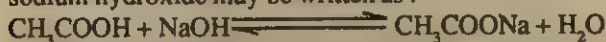
Similarly to determine the pH of a basic buffer (a weak base + its salt) the equation employed is

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \quad \dots \quad (9.28)$$

$$\text{or pH} = 14 - \text{pOH} \quad \dots \quad (9.29)$$

Exercise 9.18 : Calculate the pH of 100 cm^3 of 0.1 M acetic acid to which 50 cm^3 of 0.1 M sodium hydroxide has been added. The dissociation constant of acetic acid is 1.82×10^{-5} at 298K .

Solution : The equation for the reaction between acetic acid and sodium hydroxide may be written as :



It follows that an excess of acid will remain when 50 cm^3 of 0.1 M NaOH solution is added to 100 cm^3 of 0.1 M CH_3COOH solution; the final solution will be a mixture of sodium acetate and acetic acid. Such a mixture, composed of a weak acid and the corresponding salt of a strong alkali, will be a buffer solution.

The pH of a buffer solution, which remains approximately constant even if small amounts of acid or alkali are added, is dependent upon the relative amounts of acid and salt present in the mixture. The pH may be calculated from the equation (9.48).

50 cm^3 of 0.1 M NaOH solution would contain $\frac{50 \times 0.1}{1000} = 0.005$ moles of NaOH.

From the chemical equation above, it follows that 0.005 moles of NaOH must produce 0.005 moles of the salt, sodium acetate, and there will be an excess of 0.005 moles of acetic acid.

Since we are concerned with the ratio $[\text{Salt}]/[\text{Acid}]$, it is not necessary to convert the amounts of acid (0.005 moles) and salt (0.005 moles) to concentrations expressed in moles per litre. The concentrations will be expressed in effect as the number of moles per total volume of solution (which will be 150 cm³ approximately). Substituting the values in equation 9.27 we have

$$\text{pH} = 4.74 + \log \frac{.005}{.005} = 4.74$$

Exercise 9.19 : Calculate the amount of NH_3 and NH_4Cl needed to prepare a buffer solution of $\text{pH} = 9$ so that the total concentration of buffering reagents is 0.5 mol/L, (K_b for NH_3 at room temperature is 1.80×10^{-5} and $K_w = 10^{-14}$)

Solution : As the buffer is to be prepared from the base and its salt, it is easier to use the equation 9.28

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

For a buffer of pH equal to 9, pOH will be 5 ($\text{pH} + \text{pOH} = 14$) substituting the values in the equation 9.28,

$$5 = 4.74 + \log \frac{[\text{Salt}]}{[\text{Base}]} \quad \text{or} \quad \frac{[\text{Salt}]}{[\text{Base}]} = 1.80$$

Therefore, NH_4Cl and NH_3 should be taken in a ratio of 1.80. Now the total concentration has to be 0.50 mol/L. Let the concentration of NH_3 be x mol/L then the $[\text{NH}_4\text{Cl}] = (0.5 - x)$ mol/L

Substituting values in the above equation,

$$\frac{0.5 - x}{x} = 1.80 \quad \text{or} \quad x = 0.1786 \text{ moles}$$

Thus, 0.1786 moles NH_3 and 0.3214 moles NH_4Cl should be dissolved in one litre solution.

SELF ASSESSMENT QUESTIONS

MULTIPLE CHOICE QUESTIONS

9.1 Put a (✓) mark against the most appropriate choice :

- (i) For the gas phase reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$, the equilibrium constant K_p changes with (a) total pressure (b) catalyst (c) the amount of H_2 and I_2 present (d) temperature.
- (ii) The oxidation of SO_2 by O_2 to SO_3 is an exothermic reaction. The yield of SO_3 will be maximum if
 - (a) temperature is increased and pressure is kept constant
 - (b) temperature is decreased and pressure is increased
 - (c) both temperature and pressure are increased
 - (d) both temperature and pressure are decreased
- (iii) Two moles of NH_3 gas are introduced into a previously evacuated one litre vessel in which it partially dissociates at high temperature

$$2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$$

- At equilibrium, one mole of $\text{NH}_3(\text{g})$ remains. What is K_p ?
- (a) $27/64 \text{ mol}^2 \text{ litre}^{-2}$ (b) $3/4 \text{ mol}^2 \text{ litre}^{-2}$ (c) $3/2 = \text{mol}^2 \text{ litre}^{-2}$
 (d) $27/16 = \text{mol}^2 \text{ litre}^{-2}$
- (iv) What condition will favour the exothermic ammonia synthesis
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 (a) high temperature, high pressure (b) high temperature, low pressure,
 (c) low temperature, high pressure (d) low temperature, low pressure.
- (v) For the endothermic reaction :
 $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
 Which one of the following statements is true ?
 (a) K_c is independent of temperature (b) K_c increases as temperature increases,
 (c) K_c decreases as temperature increases, (d) K_c varies with the addition of NO
- (vi) If the equilibrium $\text{P}_4(\text{g}) + 6 \text{Cl}_2(\text{g}) \longrightarrow 4 \text{PCl}_3(\text{g})$, is attained by adding equal numbers of moles of P_4 and Cl_2 to an evacuated vessel, which of the following must be true at equilibrium ?
 (a) $[\text{Cl}_2] > [\text{PCl}_3]$ (b) $[\text{Cl}_2] > [\text{P}_4]$
 (c) $[\text{P}_4] > [\text{Cl}_2]$ (d) $[\text{PCl}_3] > [\text{P}_4]$
- vii) Consider the two gaseous equilibria involving SO_2 and O_2 , the corresponding equilibrium constants at 298K are
 $\text{SO}_2(\text{g}) + 1/2 \text{O}_2 \rightleftharpoons \text{SO}_3(\text{g}) ; K_1$
 $2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) ; K_2$
 The values of the equilibrium constants are related by
 (a) $K_2 = K_1$ (b) $K_2 = K_1^2$
 (c) $K_2 = 1/K_1^2$ (d) $K_2 = 1/K_1$
- (viii) Which one of the following mixtures is at equilibrium at a constant temperature if $K_p = 3$ for the equilibrium
 $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$
 Partial pressures of various gases are
- | | P_{NH_3} | P_{N_2} | P_{H_2} | (in atm.) |
|-----|-------------------|------------------|------------------|-----------|
| (a) | 1 | 1.5 | 1 | |
| (b) | 3 | 3 | 2 | |
| (c) | 4 | 6 | 2 | |
| (d) | 6 | 1 | 2 | |
- (ix) 1 mole of NO_2 and 2 moles of CO are enclosed in a one litre vessel to attain the following equilibrium,
 $\text{NO}_2 + \text{CO} \rightleftharpoons \text{NO} + \text{CO}_2$
 It was estimated that at equilibrium 25% of initial amount of CO is consumed. The equilibrium constant K_p is
 (a) $1/4$ (b) $1/3$ (c) $1/2$ (d) 1
- (x) What will be the units of K_p for a gas phase equilibrium of the following reaction
 $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{NOCl}(\text{g})$
 (a) mol dm^{-3} (b) mol dm^{-1} (c) $\text{dm}^3 \text{mol}^{-1}$ (d) being a ratio, it would have no units.
- (xi) Which of the following reactions has the least tendency to go to completion ?
 (a) $2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) K = 4.7 \times 10^{-4}$
 (b) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g}) K = 3.2 \times 10^{16}$
 (c) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) ; K = 5.0 \times 10^{-11}$
 (d) $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g}) ; K = 1.7 \times 10^{27}$
- (xii) When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with
 (a) $10^{-4} \text{M}(\text{Ag}^+)$ and $10^{-4} \text{M}(\text{Cl}^-)$
 (b) $10^{-6} \text{M}(\text{Ag}^+)$ and $10^{-6} \text{M}(\text{Cl}^-)$

- (c) $10^{-4}M$ (Ag^+) and $10^{-4}M$ (Cl^-)
 (d) $10^{-4}M$ (Ag^+) and $10^{-4}M$ (Cl^-)
- (xiii) Amongst the trihalides of nitrogen, which one is least basic
 (a) NF_3 , (b) NCl_3 , (c) NBr_3 , (d) NI_3
- (xiv) A certain buffer solution contains equal concentration of HX and X^- . The K_a for HX is 10^{-6} . The pH of the buffer is
 (a) 4 (b) 7 (c) 10 (d) 14
- (xv) Which of the following salt solutions is basic?
 (a) $HOCl$ (b) $NaOCl$ (c) $NaHSO_4$ (d) NH_4NO_3
- (xvi) The pH of a 10^{-8} molar solution of HCl in water is
 (a) 8 (b) 7 (c) between 6 and 7 (d) between 7 and 8
- (xvii) A certain weak acid has a dissociation constant of 1.0×10^{-4} . The equilibrium constant for its reaction with a strong base is
 (a) 1.0×10^{-4} (b) 1.0×10^{-10} (c) 1.0×10^{10} (d) 1.0×10^{14}
- (xviii) According to Lowry-Bronsted concept the relative strength of the bases CH_3COO^- , OH^- and Cl^- follows the order
 (a) $CH_3COO^- > OH^- > Cl^-$
 (b) $OH^- > CH_3COO^- > Cl^-$
 (c) $CH_3COO^- > Cl^- > OH^-$
 (d) $OH^- > Cl^- > CH_3COO^-$
- (xix) The expression for the solubility product of CaF_2 is K_{sp} is
 (a) $[Ca^{2+}] [2F^-]$ (b) $[Ca^{2+}] [F^-]^2$ (c) $[Ca^{2+}] [F^-]$ (d) $[Ca^{2+}] [2F^-]^2$
- (xx) Let the solubility of $AgCl$ in water, in $0.01M$ $CaCl_2$, in $0.01M$ $NaCl$ and in $0.05M$ $AgNO_3$ be S_1 , S_2 , S_3 and S_4 respectively. The correct order of these solubilities is
 (A) $S_1 > S_2 > S_3 > S_4$
 (B) $S_1 > S_3 > S_4 > S_2$
 (C) $S_1 > S_2 = S_3 > S_4$
 (D) $S_1 > S_3 > S_4 > S_2$

2

Fill in the blanks

- (i) If matter neither enters a system, nor leaves it, the system is
- (ii) Constancy of macroscopic properties in a/an system represents a steady state.
- (iii) Vapour pressure of a pure solvent is always ... than that of the ideal solution
- (iv) Equilibrium is a ... state. At equilibrium R_p and R_c are ...
- (v) According to the law of mass action the reaction quotient Q is at the equilibrium state.
- (vi) For a reaction the value of K_p is equal to K_c at constant temperature if ... for the reaction.
- (vii) For deliquescence to occur, the vapour pressure of water in air must ... the vapour pressure of pure salt.
- (viii) For a particular reaction the value of equilibrium constant can be changed by
- (ix) In the reaction



A^- functions as a/an

- (x) pH of $10^{-5}M$ $NaOH$ is

3

Point Out the Correct Statements of the Following

- (i) When a liquid and its vapours are in equilibrium and the pressure is suddenly decreased, cooling occurs.
- (ii) The solubility of a gas decreases in water as the pressure of the gas above water increases.
- (iii) Le Chatelier's principle predicts that an endothermic change will be favoured at high temperature.

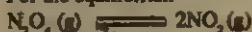
(iv) A catalyst decreases the value of equilibrium constant of an exothermic reaction.

(v) The equilibrium



shifts to the left at constant temperature if the volume of the container is increased.

(vi) For the equilibrium



at any given temperature, the quotient $\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$ is constant.

(vii) For the equilibrium



the expression for K_c is $\frac{[\text{H}_2\text{O}(\text{l})]}{[\text{H}_2(\text{g})]}$

(viii) K_{sp} for AgCl is 1.21×10^{-10} . The solubility of AgCl in water is $1.1 \times 10^{-5} \text{ mol L}^{-1}$.

(ix) A buffer is obtained if 0.4 mol of ethanoic acid is mixed with 0.2 mol of NaOH .

(x) H_3O^+ and OH^- is a conjugate acid - base pair.

Match the following choosing one item from Column X and the appropriate item from Column Y

Column 'X'

- (A) Bronsted acid
- (B) Buffer solution
- (C) Closed system
- (D) Equilibrium state
- (E) Heterogeneous system
- (F) Ionic product of water
- (G) Irreversible reaction
- (H) Low vapour pressure
- (I) p^H
- (J) Lewis base

Column 'Y'

- (i) high boiling point
- (ii) Cl^-
- (iii) $p^H - p^{OH}$
- (iv) NH_4^+
- (v) 0.4 mol CH_3COOH + 0.2 mol NaOH
- (vi) $\text{AgNO}_3 + \text{NaCl} \rightarrow \text{AgCl} + \text{NaNO}_3$
- (vii) matter does not exchange between the system and the surroundings
- (viii) $\Delta G = 0$
- (ix) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
- (x) 1.0×10^{-14}

SHORT ANSWER QUESTIONS

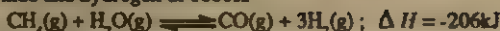
Give answer in one or two sentences for each of the followings

- (i) Why a bottle of liquor ammonia should be cooled before opening the stopper?
- (ii) Why a cook does not cry as much when cutting onions taken out from the freezer as when cutting a warm one?
- (iii) Consider a reaction mixture

$$\text{PbCl}_2(\text{s}) + \text{C}_2\text{O}_4^{2-} (1.0 \times 10^{-2} \text{ M}) \rightleftharpoons \text{PbC}_2\text{O}_4(\text{s}) + 2\text{Cl}^- (0.5 \text{ M})$$
 is at equilibrium at 298K. What would be the effect on the concentration of $\text{C}_2\text{O}_4^{2-}$ if some NaCl solution was added to the equilibrium mixture?
- (iv) Write the concentration quotient for the reactions,
 - (a) $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})$
 - (b) $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- (v) Consider the equilibrium

$$\text{CO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{COCl}_2(\text{g})$$
 at constant temperature, predict the direction to which the system would shift if the pressure is increased by decreasing the volume of the container.
- (vi) Consider the following reaction between methane and steam to form carbon

monoxide and hydrogen at 1000K



Predict what would happen to the equilibrium concentration of hydrogen if

- (i) temperature is increased
- (ii) the pressure of the equilibrium mixture is increased.
- (iii) a catalyst is added.
- (vii) How will the pH change if 500 cm³ 0.2M HCl is diluted to 1 litre solution?
- (viii) Solution of the electrolyte MX is saturated or unsaturated if $[\text{M}^{+}][\text{X}^{-}] > K_{\text{sp}}$.
- (ix) Write balanced equations for the hydrolysis of (a) P^{3-} (b) NH_4^{+} . Indicate the pH of the aqueous solutions.
- (x) What is the concentration of H^{+} ions in a 0.1M solution of hypochlorous acid, HOCl ($K_{\text{a}} = 5 \times 10^{-8}$).

TERMINAL QUESTIONS

- 9.1 Write an equilibrium constant expression, K_{A} , for each of the following reactions?
 - (a) $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
 - (b) $\text{NH}_3(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{NO}(\text{g}) + \text{N}_2\text{O}(\text{g})$ (Not balanced)
 - (c) $2\text{NaHCO}_3(\text{s}) \rightleftharpoons \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
 - (d) $\text{CO}_2(\text{s}) \rightleftharpoons \text{CO}_2(\text{g})$
 - (e) $\text{CS}_2(\text{l}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{CCl}_4(\text{l}) + \text{S}_2\text{Cl}_2(\text{l})$ (not balanced)
 - (f) $\text{Ag}_2\text{CrO}_4(\text{s}) \rightleftharpoons 2\text{Ag}^{+}(\text{aq}) + \text{CrO}_4^{2-}(\text{aq})$
- 9.2 Write an equilibrium constant expression K_{p} , for each of the following equilibria?
 - (i) $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$
 - (ii) $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
 - (iii) $\text{P}_4\text{O}_{10}(\text{g}) + 6\text{PCl}_5(\text{g}) \rightleftharpoons 10\text{POCl}_3$
 - (iv) $2\text{H}_2\text{S}(\text{g}) + 3\text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}(\text{g}) + 2\text{SO}_2(\text{g})$
- 9.3 What is meant by a dynamic equilibrium?
- 9.4 Arrange the following reactions in the order of their decreasing tendency to proceed toward completion.
 - (i) $4\text{NH}_3(\text{g}) + 3\text{O}_2(\text{g}) \rightleftharpoons 2\text{N}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$ $K_{\text{c}} = 1 \times 10^{200}$
 - (ii) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ $K_{\text{c}} = 5 \times 10^{38}$
 - (iii) $2\text{HF}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{F}_2(\text{g})$ $K_{\text{c}} = 1 \times 10^{200}$
- 9.5 Explain in brief the relationship between -
 - (i) the rates of chemical reactions and the equilibrium constant
 - (ii) the equilibrium constants K_{c} and K_{p}
 - (iii) the reaction quotient, Q , and the equilibrium constant expression K_{c}
- 9.6 In a 5 litres flask, 2 mol O_2 , 1 mol SO_2 and 4 mol SO_3 are enclosed at 500K. If K_{c} for the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ is 100 at 500K. Can the above mixture be maintained indefinitely at 500K? If not, in which direction will the reaction occur?
- 9.7 Identify each of the following as Arrhenius acids or bases. For each, write a chemical reaction to show its reaction with water. Indicate the pH of aqueous solution (i) CaO (ii) O^{2-} (iii) HF
- 9.8 Hydrogen sulphide is a stronger acid than phosphine, PH_3 . What would you conclude about the strengths of their conjugate bases, HS and PH_2 ?
- 9.9 Which would be expected to be a stronger Lewis base, NH_3 or NF_3 ? Explain.
- 9.10 How is p^{H} defined? How is p^{OH} defined? Why does $\text{p}^{\text{H}} + \text{p}^{\text{OH}} = 14$?
- 9.11 For the reaction $\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$ at 440K the

equilibrium concentrations Ml^{-3} are

$[\text{H}_2\text{O}] = 0.45$; $[\text{CO}] = 0.60$

$[\text{H}_2] = 0.50$ and $[\text{CO}_2] = 0.42$

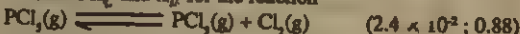
What is the value of K_c (Ans. $K_c = 0.78$)

9.12

A 1.0 litre reaction flask containing the equilibrium mixture $\text{CO} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2$ was found to contain 0.40 mol of COCl_2 , 0.10 mol of CO , and 0.50 mol of Cl_2 . If 0.30 mol of CO is added at constant temperature, what will be the new concentrations of each component at equilibrium? ($[\text{CO}] = 0.22\text{M}$; $[\text{Cl}_2] = 0.32\text{M}$; $[\text{COCl}_2] = 0.58\text{M}$)

9.13

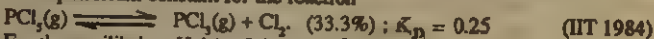
At 450K an equilibrium mixture of PCl_5 , PCl_3 and Cl_2 in a 5 litre container consists of 0.50 mol PCl_5 , 0.15 mol PCl_3 , and 0.40 mol Cl_2 . Calculate K_c and K_p for the reaction



9.14

One mole of N_2 and 3 moles of PCl_5 are placed in a 100 litre vessel heated to 500K. The equilibrium pressure is 2.05 atm.

Assuming ideal behaviour, calculate the degree of dissociation for PCl_5 and equilibrium constant for the reaction



9.15

For the equilibrium $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

The equilibrium constant K_c is 50 at 500K.

What will be the equilibrium concentrations if 1 mol $\text{H}_2(\text{g})$, 2 moles $\text{I}_2(\text{g})$ and 3 moles $\text{HI}(\text{g})$ are enclosed in a 1 litre evacuated vessel and the reaction mixture is heated to 500K?

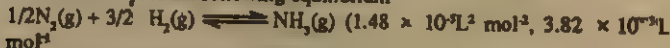
Ans. ($[\text{H}_2] = 0.30\text{ mol}$; $[\text{I}_2] = 1.70\text{ mol}$; $[\text{HI}] = 4.40\text{ mol}$)

9.16

One mole of N_2 is mixed with 3 moles of H_2 in a 4L container. If 0.25% of N_2 is converted to ammonia by the following reaction -



Calculate the equilibrium constant K_c in concentration units. What will be the value of K_c for the following equilibrium



9.17

What is the hydroxide ion concentration in a solution whose p^{H} is 10.2? (1.58×10^{-14})

9.18

The solubility products of CaC_2O_4 and Na_3AlF_6 are the same (4×10^{-10}). Which of these salts will be more soluble in water? (Na_3AlF_6)

9.19

The solubility product of lead bromide is 8×10^{-6} . If the salt is 80% dissociated in saturated solution, find the solubility of the salt. (12.44 g L^{-3})

9.20

What is the percentage hydrolysis of NaCN in N/80 solution when the dissociation constant for HCN is 1.3×10^{-9} and $K_w = 10^{-14}$? (2.48)

9.21

When water is saturated with $\text{Ca}(\text{OH})_2$, the observed p^{H} of the solution is 12.137. Calculate the solubility product of $\text{Ca}(\text{OH})_2$. (1.29×10^{-6})

9.22

Calculate the concentration of H_3O^+ ions in a solution of acetic acid with $K_a = 1.8 \times 10^{-5}$. Given that the acid is 0.3% ionized at the given concentration. ($6 \times 10^{-3}\text{M}$)

9.23

pK value for acetic acid is 4.76 at room temperature. How will you obtain a buffer of pH value 5.40 from acetic acid and sodium acetate?

9.24

What will be pH of a solution obtained by dissolving 5g acetic acid and 7.5 g of sodium acetate in water and making the volume equal to 500 mL ($K_a = 1.8 \times 10^{-5}$ at 298K)? (4.78)

9.25

The dissociation constant of a weak acid HA is 4.9×10^{-4} . After making the necessary approximation, calculate

(i) percentage ionization

- (ii) p_{H^+} and (iii) OH^- concentration in a decimolar solution of the acid.
Water has pH of 7 (IIT 1983)

(ii) 0.07%; (ii) 4.16; (iii) $1.43 \times 10^{-4} M$

ANSWERS TO SELF ASSESSMENT QUESTIONS

- 9.1 (i) d (ii) b (iii) d (iv) c (v) b (vi) c (vii) c (viii) c (ix) b (x) c (xi) c (xii) a (xiii) a (xiv) c (xv) b (xvi) c (xvii) c (xviii) b (xix) b (xx) b
- 9.2 (i) a closed system
(ii) an open
(iii) more
(iv) dynamic, equal
(v) equal to equilibrium constant
(vi) Δn is equal to zero
(vii) exceed
(viii) changing the temperature
(ix) base
(x) ~~base~~
- 9.3 (i) T (ii) F (iii) T (iv) F (v) F (vi) T (vii) F (viii) T (ix) T (x) F
- 9.4 (A) (iv) ; (B) (v) ; (C) (vii); (D) (viii) ; (E) (ix) ; (F) (x) ; (G) (vi) ; (H) (i); (I) (iii) (J) (ii)
- 9.5 (i) Vapour pressure of ammonia inside the bottle is reduced on cooling.
(ii) At low temperature vapour pressure is also low.
(iii) Concentration of $C_2O_4^{2-}$ ions would increase.
(iv) (a) $Q = \frac{[NOCl]^2}{[NO]^2 [Cl_2]}$
(b) $Q = p_{CO_2}$
(v) There is decrease in volume when the reaction proceeds in the forward direction, thus increase in pressure would shift the reaction to forward direction.
(vi) (i) $[H_2]$ decreases
(ii) $[H_2]$ decreases
(iii) $[H_2]$ unaffected
(vii) pH increases from 0.699 to 1.0
(viii) Saturated
(ix) (a) $F^- + H_2O \rightleftharpoons HF + OH^-$ ($K_a > 1$)
(b) $NH_4^+ + 2H_2O \rightleftharpoons NH_3 + H_3O^+$ ($K_a < 1$)
(x) $[H^+] = \sqrt{K_a C} = \sqrt{5.0 \times 10^{-4} \times 0.1}$
 $= 7.1 \times 10^{-3} \text{ mol L}^{-1}$

UNIT 10

Redox Reactions

.....Upon this principle the whole art of making experiments in chemistry is founded : we must always suppose a true equality between the principles of the body which is examined and those which are obtained on analysis.

Antoine Laurent Lavoisier
(1743-1794)

UNIT PREVIEW

- 10.1 Introduction
- 10.2 Oxidation and reduction as an electron transfer process
 - 10.2.1 Oxidation and reduction
 - 10.2.2 Electrode reaction
- 10.3 Redox reactions in aqueous solution - electrochemical cells
 - 10.3.1 Salt bridge and its functions
 - 10.3.2 Conventional representation of galvanic cells
- 10.4 EMF of a Galvanic cell
 - 10.4.1 Concept of electrode potential
 - 10.4.2 Types of single electrodes
 - 10.4.3 Experimental measurement of electrode potential
 - 10.4.4 Measurement of EMF of a cell using potentiometer
 - 10.4.5 Electrochemical series
 - 10.4.6 Applications of electrochemical series
- 10.5 Other voltaic cells
- 10.6 Dependence of EMF on concentration and temperature
 - 10.6.1 The electrode potential
 - 10.6.2 The cell potential
 - 10.6.3 Electrical units
 - 10.6.4 Electrical work and free energy change
 - 10.6.5 Equilibrium constant and standard cell potential
- 10.7 Electrolysis
 - 10.7.1 Electrolysis of acidified water
 - 10.7.2 Laws of electrolysis
 - 10.7.3 Applications of electrolysis
- 10.8 Oxidation number
 - 10.8.1 Redox reactions in terms of oxidation number
 - 10.8.2 Oxidation and nomenclature
 - 10.8.3 Balancing of oxidation and reduction reactions
 - 10.8.4 Applications of redox reactions

Self assessment questions

Terminal questions

Answers to self assessment questions

LEARNING OBJECTIVES

- At the completion of this unit, you should be able to :
1. Understand the meaning of oxidation and reduction as applied to chemical changes.

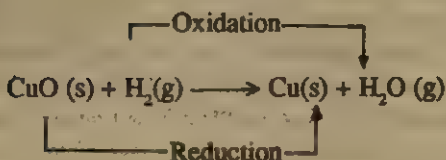
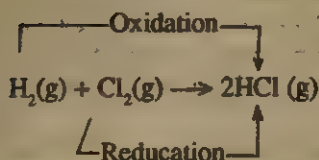
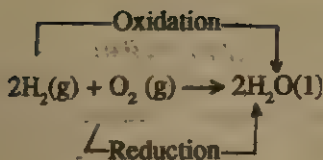
2. Describe an electrochemical cell as composed of an oxidation and a reduction half-reactions physically separated so that electron transfer occurs through an external circuit from the anode (oxidation) to the cathode (reduction).
3. Sketch the electrochemical cells (galvanic cell) to show the anode and cathode, the half-cell reactions and the direction of electron and ion flow.
4. Relate the EMF (emf) of a cell to the difference between the potentials of the two half-cells.
5. Define standard electrode potential in relation to the standard hydrogen electrode.
6. Calculate cell potential from electrode potentials.
7. Account for the dependence of emf of a cell on concentration and temperature.
8. Describe the phenomenon of electrolysis
9. State the laws of electrolysis
10. Distinguish between the electrochemical cell and the electrolytic cell.
11. Understand the meaning of oxidation number and its significance.
12. Use half-reaction equations to balance oxidation - reduction equations.
13. Use the oxidation number for balancing a chemical equation.
14. Emphasize the importance of redox reactions.
15. Appreciate the mutual exchange of electrons in redox reactions.

10.1 INTRODUCTION

The type of chemical reactions described as oxidation-reduction often contracted to redox is a subject of great importance in chemistry. Chemical reactions are a source of energy as the elements tend to gain or lose electrons in the drive towards stability.

Burning of coal, combustion of petrol in an automobile engine *etc.* are oxidation reactions. So is the burning of food by our bodies. But all oxidation reactions are accompanied by reduction reactions. We hear a lot about explosions, fires, corrosion, *etc.* Science has made progress towards the development of electrochemical cells, protection of metals against corrosion, modern dental and surgical methods and a growing understanding of the use and production of energy from fuels and foods. All of these processes involve oxidation-reduction reactions.

Addition of oxygen to a substance gives the oxide of that substance. For example, oxygen reacts with carbon, sulphur and phosphorus and forms carbon dioxide, sulphur dioxide and phosphorus pentoxide respectively. In a similar way hydrogen combines with oxygen and chlorine, their binary compounds - water and hydrogen chloride are produced. All such reactions are also called redox reactions. As the name implies, the term oxidation was originally used just to describe the addition of oxygen to a substance. Thus, all examples of burning involve oxidation. Since hydrogen was in many ways regarded as a chemical opposite to oxygen, the definition of oxidation was later extended to include the removal of hydrogen from a compound. Reduction is in all respects the opposite of oxidation. Thus, reduction is the removal of oxygen from or the addition of hydrogen to a substance. These views are well explained by the following examples :



The substance that furnishes oxygen or removes hydrogen is called an oxidizing agent (oxidant). Oxygen, chlorine and cupric oxide involved in the above reactions are, thus, oxidizing agents. These substances have been reduced in the reactions. Similarly a substance that supplies hydrogen or removes oxygen is a reducing agent (reductant). Hydrogen, thus, acts as a reducing agent in the reactions portrayed above. It has been oxidized in all the above reactions.

10.2 OXIDATION AND REDUCTION AS AN ELECTRON TRANSFER PROCESS

All the reactions you have come across involve the loss and gain of electrons. When a metal reacts, the lattice loses electrons, forming positive ions. The electrochemical series tells you how easily this process takes place when metals react with water, acids or solutions of other metal salts. These electrons lost from the metal atoms may be consumed by :

- hydrogen atoms in water or acids,
- the ions of a less reactive metal, or
- the atoms of a nonmetal

When nonmetals react, their atoms accept electrons, and thereby become negative ions. These electrons, gained or accepted by the nonmetal atoms have been lost (or supplied) from :

- metal atoms, or
- less reactive nonmetal ions.

So all these reactions involve the transfer of electrons from the atoms or ions of one element to the atoms or ions of another element when one

species loses electrons another gains them.

10.2.1 OXIDATION AND REDUCTION

Oxidation is the loss of electrons by atoms, ions or molecules and reduction is the gain of electrons by atoms, ions or molecules. Since there cannot be a net loss or gain of electrons in a chemical reaction - only a transfer among substances - oxidation and reduction must always occur as concurrent reactions in equivalent amounts. Such coupled reactions are called redox reactions. A large number of redox reactions are possible which arise from various combinations of pairs of oxidants and reductants.

Any substance that promotes the loss of electrons because of its tendency to gain them is called an oxidizing agent. Any substance that readily gives up its electrons is called a reducing agent. Thus, in a reaction oxidizing agents get reduced and reducing agents are oxidized. Under the circumstances, the oxidation state of any substance may be used to predict the tendency of a material to act as an oxidising agent or a reducing agent. A knowledge of common oxidizing agents and reducing agents can help us design reactions in which selected substances can be oxidized or reduced.

Consider the reaction between zinc metal and copper (II) sulphate solution and also between copper metal and silver nitrate solution. The zinc strip is immersed in a solution of copper sulphate contained in a beaker A (Fig. 10.1) and the copper strip is placed in a solution of silver nitrate contained in a beaker B (Fig. 10.2). We observe some reactions in the beakers and allow them to proceed for some time say 5 minutes. After 5 minutes we observe some metallic deposit on the two strips.

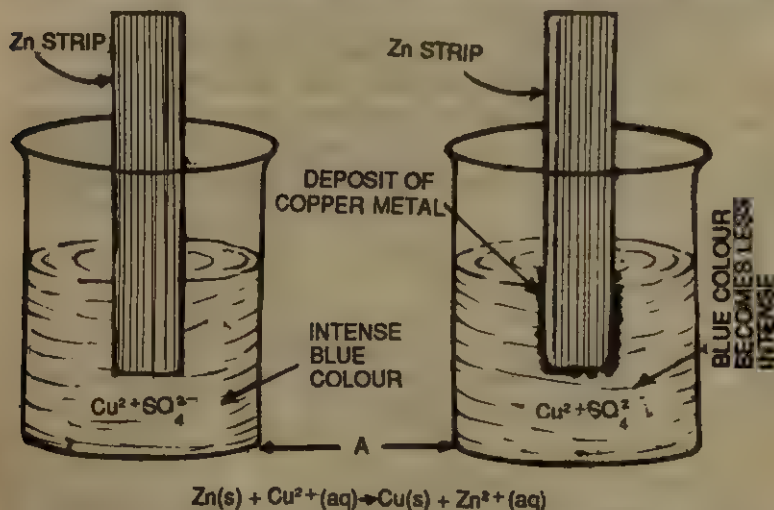


Fig. 10.1 Behaviour of zinc towards aqueous solution of copper sulphate
Why does this change take place on the metallic surface ? This is an

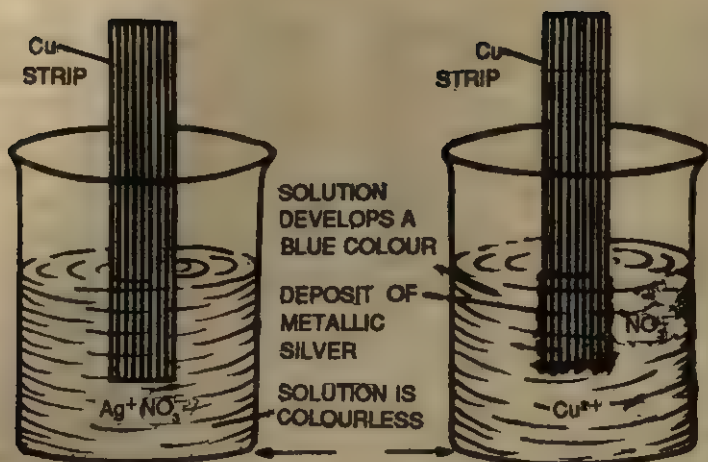
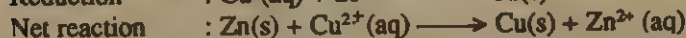
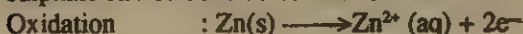
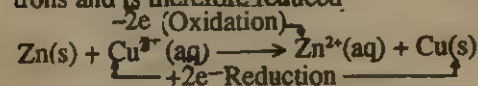


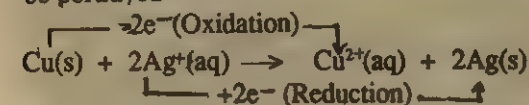
Fig. 10.2 Behaviour of copper towards aqueous solution of AgNO_3 , oxidation-reduction reaction. The reaction of zinc metal with copper sulphate can be considered in two half-reactions.



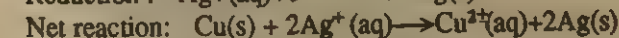
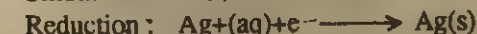
Zinc loses electrons and is therefore oxidized and Cu^{2+} ion gains electrons and is therefore reduced.



In this reaction Cu^{2+} ions are displaced from the solution which after accepting electrons get deposited on the zinc strip. Similarly the displacement of silver from silver nitrate in the presence of copper strip can be portrayed



This is an oxidation-reduction which can be considered in two half reactions.



On the other hand if a copper plate is immersed in a solution of $\text{Zn(NO}_3)_2$ (or ZnSO_4) no reaction takes place (Fig. 10.3).

Why does copper behave differently towards Ag^+ and Zn^{2+} ions ? The

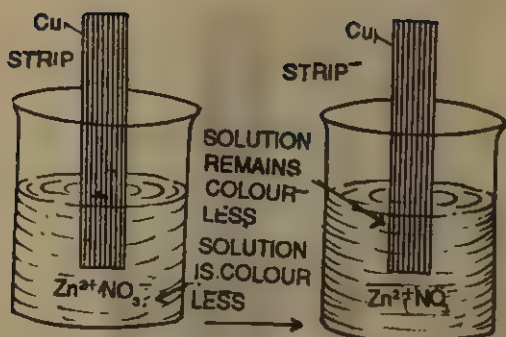


Fig. 10.3 Behaviour of copper towards aqueous solution of ZnNO_3

reduction tendencies is essential in understanding the direction of spontaneous change in redox reactions.

10.2.2. Electrode Reaction

There are three possibilities when a metal plate (M) is immersed in a solution containing the M^{n+} ions (Fig. 10.4).

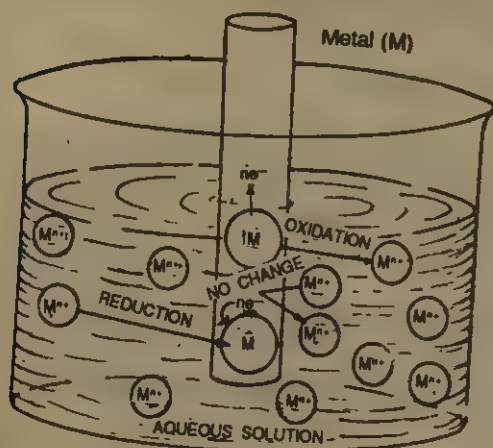
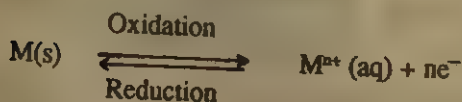


Fig. 10.4 Electrode equilibrium



answer to this lies with the relative tendency of accepting electrons by Ag^+ and Zn^{2+} ions. Obviously Ag^+ ions have a greater tendency to gain electrons (a greater tendency towards reduction) than Zn^{2+} ions. Thus, a fair knowledge of relative oxidation and

- (i) A metal ion M^{n+} may come in the contact of the electrode and experience no change.
- (ii) A metal ion M^{n+} may come in the contact of the electrode, accept n electrons and be reduced to a metal atom M .
- (iii) A metal atom on the electrode M may oxidize and thereby lose n electrons to the electrode and enter the solution as M^{n+} .

When dynamic equilibrium is attained, a small difference in electrical

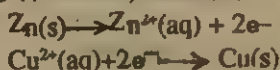
potential exists between the metal electrode and the solution. A metal with a strong tendency of losing electrons, imparts M^{n+} ions to the solution resulting in a fractional increase in the number of metal ions, M^{n+} in the solution and a fractional increase in the number of electrons on the electrode. As a result, the electrode develops a small negative potential with respect to the solution.

It is, however, possible to present the above picture for two different metals, e.g., copper and zinc. Two electrodes are immersed in their salt solutions and a contact is maintained indirectly both between electrodes and solutions (Fig. 10.5). This allows the flow of electric current. Electrons migrate (through a connecting wire) from the zinc electrode to the copper electrode and Cu^{2+} ions as illustrated in Fig. 10.5. Zn has a stronger tendency to lose electrons than copper. Thus, oxidation occurs at the zinc electrode (anode) and reduction occurs at the copper electrode (cathode).

Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (i) occurs more readily than $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ (ii)

Reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ (iii) occurs more readily than $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ (iv)

Thus, combining (i) and (iii) reactions.



Redox change : $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

The redox change occurring in such a fashion is called an electrochemical change.

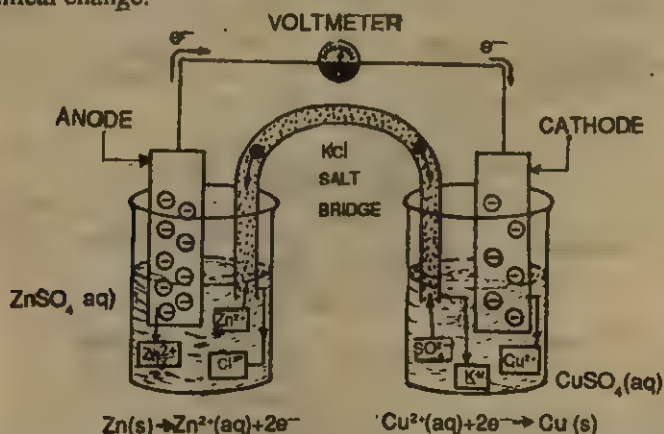


Fig 10.5 An assembly showing an electrochemical change. A difference in potential is established between the two metal electrodes. Electrical contact between the solutions is established through a salt bridge that allows the migration of ions but not that of solutions. Electrons migrate through the wire connecting the electrodes externally. Thus a complete circle is established.

10.3 REDOX REACTIONS IN AQUEOUS SOLUTIONS - ELECTROCHEMICAL CELLS

Electrochemical cell is based on the physical separation of oxidizing and reducing agents in a system that permits the free migration of ions between the two and an external flow of electrons. For example, when we plan a physical arrangement that promotes the electrons transfer tendencies between zinc and copper ions indirectly through an external metal wire, an electricity producing phenomenon will result. Such a system is called an electrochemical cell. Its direct contact occurs between the oxidizing and reducing agents, a primitive short circuit will result. The separation can be achieved by using a salt bridge or porous barrier.

Thus, in electrochemical cells, chemical reactions are used to supply electrical energy. A metal strip dipping in a solution is known as a half-cell or an electrode. The reaction that takes place in a half-cell is known as half-cell reaction. When two half-cells are connected internally by a salt bridge or a porous diaphragm and externally by a conductor, this assembly will constitute an electrochemical or galvanic cell or voltaic cell (Fig. 10.6). To understand how a reaction produce electrical energy, the oxidation-reduction reaction of the cell (Fig. 10.6) is resolved into two partial equations.

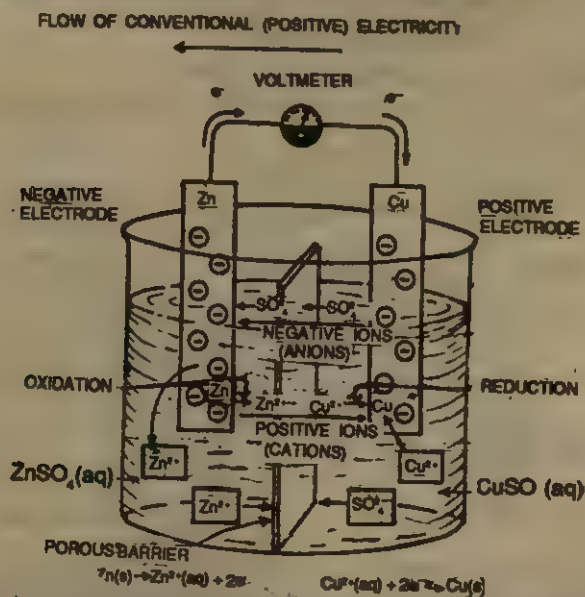


Fig. 10.6 A diagrammatic view of a zinc-copper electrochemical cell with a porous diaphragm or partition to prevent the mixing of two electrolytes contained in the cell

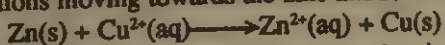
At the zinc electrode : $\text{Zn(s)} \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$. This electrode, being rich in electrons, is assigned negative polarity. It pushes electrons into the external circuit.

At the copper electrode : $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu(s)}$

This electrode is assigned positive polarity.

Electrons flow between the two electrodes across which a potential difference exists. They flow from a couple (M^{n+}/M) of higher potential to a couple of lower potential.

As reactions proceed, the electrolyte around the zinc electrode becomes rich in Zn^{2+} ions due to dissolution of zinc electrode (oxidation) and the electrolyte around the copper electrode becomes deficient in Cu^{2+} ions due to the reduction of Cu^{2+} ions. Electrical neutrality is maintained by cations moving into the region around the copper cathode and by anions moving towards the zinc anode. The overall reaction is :



Thus, the energy liberated by the reaction is used to do some electrical work rather than being lost as heat.

Since the ions in the solution of ZnSO_4 (aq) are free to migrate through the porous barrier, oxidation and reduction take place until one electrode (Zn strip) accumulates as many electrons at it can, while the other electrode (Cu strip) has lost an equal number of electrons. At this stage, when the difference in electron pressure is maximum, it is said that an EMF (electromotive force) has been developed. For this phenomenon some other words like voltage, potential and potential difference can also be used.

The increase in the number of electrons on the zinc strip and the simultaneous decrease in the number of electrons on the copper strip is portrayed through Fig. 10.7.

The terms anode and cathode are assigned according to the direction of ion flow. The anode attracts anions and the cathode attracts cations.

The Fig. 10.6 shows the movement of negatively charged ions (anions) towards the zinc strip and the movement of positively charged ions (cations) towards the copper strip which makes the zinc strip the anode and the copper strip the cathode respectively. Hence, the terms anodic oxidation, and cathodic reduction are used in connection with the cell. Figure 10.8 portrays the electrode labelling.

If these electrodes are weighed before and after the chemical reaction, it will be found that Zn electrode has lost its mass while Cu electrode has gained its mass. This is due to the fact that Zn electrode which acts as anode produces Zn^{2+} ions in solution, and thus, reduces in size. At the Cu electrode there is a reduction reaction, Cu deposits on the electrode, and thus, it grows in size when the cell is in operation.

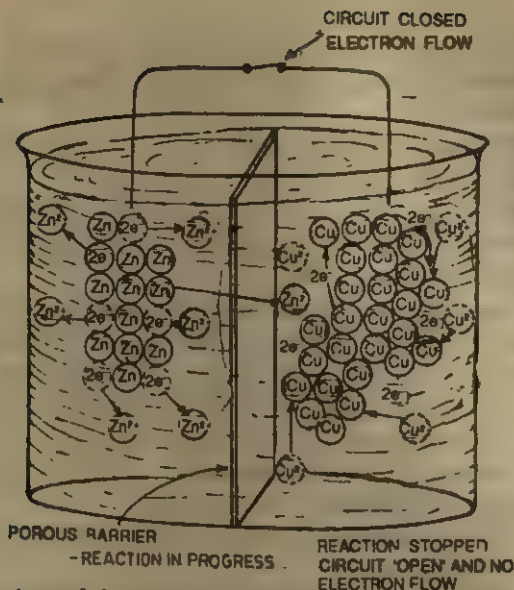


Fig. 10.7(A) A view of the zinc strip disappearance as zinc atoms lose electrons (oxidation)

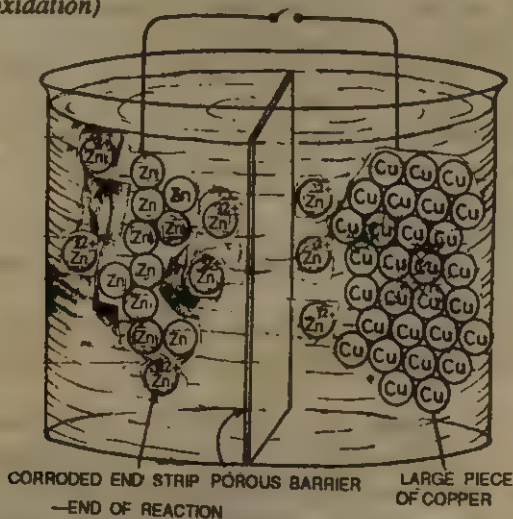


Fig. 10.7 (B) The increase in the mass of copper strip as copper ions gain electrons (reduction) in the change to copper atoms

Electrons do not appear in the net cell reaction because electrons which are set free at the zinc electrode (anode) travel through the external circuit and are accepted at the copper electrode (cathode).

10.3.1 Salt Bridge and its Functions

The saturated solution of salt (e.g., KCl , KNO_3 or NH_4NO_3) mixed with gelatin or agar gel is filled in a glass tube (bent according to requirement) which connects the two electrolytes like a bridge, hence,

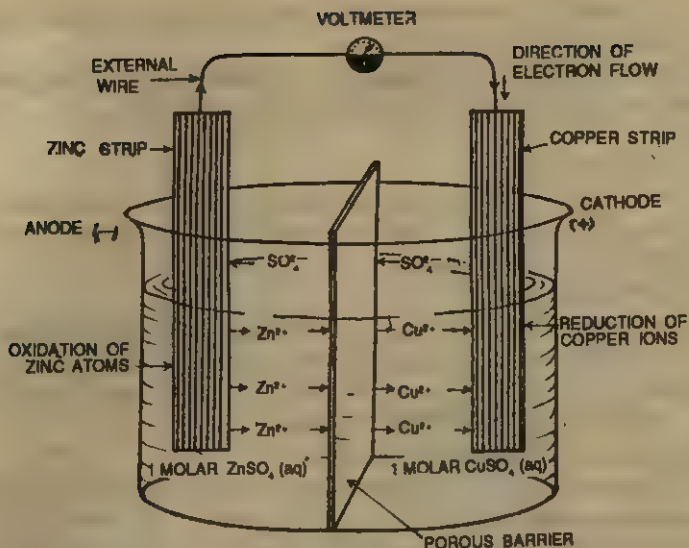


Fig. 10.8 The labelling of the electrode depends upon the oxidation and reduction sites and the ultimate direction of ion flow.

the name salt bridge. This does not permit bulk flow of solution between compartments but allows the migration of ions to establish an electrical current through the electrolytes.

In the presence of salt bridge (Fig. 10.5), the negative ions move from the cathode compartment through salt bridge to anode compartment. The positive ions move in the reverse direction. Thus, the salt provides cations and anions to replace the ions lost or produced at the two electrodes. For example, in the anode compartment, additional Zn^{2+} ions appear which are balanced by Cl^- ions supplied by the salt bridge. Similarly, in the cathode compartment additional SO_4^{2-} ions appear due to the reduction of Cu^{2+} ions. The SO_4^{2-} ions are balanced by K^+ ions supplied by the salt bridge.

10.3.2 Conventional Representation of Galvanic Cells

Galvanic cells are generally described by a notation which simplifies their description. A galvanic cell is considered as an assembly of two half-cells. The various notations used for the two half-cells are as follows:

(i) The electrode and the electrolyte are separated either by a semicolon (;) or a single vertical line (|)

$\text{Zn}; \text{Zn}^{2+}$ or $\text{Zn} | \text{Zn}^{2+}$

Similarly for another half-cell,

$\text{Ag}, \text{AgCl}; \text{Cl}^-$ or $\text{Ag} + \text{AgCl} | \text{Cl}^-$

The sign of comma or plus interposed between Ag and AgCl shows that the two substances together form the electrode. Electrolytes may be shown either by ionic species or by the chemical formulae. To

be more specific, concentration may also be shown in bracket, e.g., $\text{Zn} \mid \text{Zn}^{2+} (0.1\text{M})$ or $\text{Zn} \mid \text{ZnSO}_4 (0.1\text{M})$

(ii) The salt bridge connecting the two solutions is represented by a double vertical line (\parallel) between them. For example, for a zinc-copper cell,



The porous diaphragm is also shown by a double vertical line (\parallel).

(iii) The anode half-cell is written on the left hand side and the cathode half-cell on the right-hand side.



(iv) The strength of solutions, pressure of gases, and physical state of the solid or liquid used in cells are shown by appropriate notations within brackets, e.g., $\text{Pt(s)}, \text{H}_2(\text{g}, 1 \text{ atm}); \text{H}^+ (a = 0.1) \parallel \text{Cu}^{2+} (a = 0.1); \text{Cu(s)}$

10.4 EMF OF A GALVANIC CELL

10.4.1 Concept of Electrode Potential

The oxidizing power or reducing power of an electrode can be determined experimentally by means of a galvanic cell. In such a cell the reaction takes place spontaneously because one atom or ion attracts electrons more strongly than another atom or ion. The phenomenon of a metal passing into solution as metal ions and liberating the electrons ($\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$) is called de-electronation and the electrode where it occurs is known as the oxidation electrode or anode. The reverse process of the gain of electrons by an ion with the discharge of metal ($\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$) is called electronation. The electrode where it occurs is called reduction electrode or cathode.

Electrons released accumulate on the metal electrode and cations, thus, produced exist in the surrounding solution. This results in the formation of electrical double layer at the electrode (Fig. 10.9). Thus, a

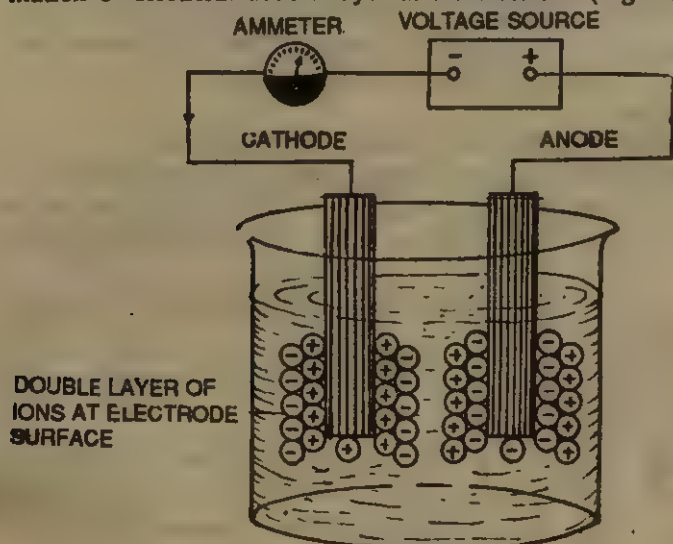
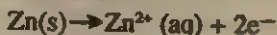


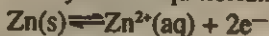
Fig. 10.9 Electrical double layer

difference in potential exists at the surface of the metal electrode dipped in its salt solution. This is called electrode potential.

A small piece of zinc metal on immersing in its salt solution loses some electrons.



Now in the absence of some agency to which these electrons could be transferred, they will be attracted by the zinc ions again forming atoms. A dynamic equilibrium is established almost immediately.



It is, therefore, a single electrode cannot constitute a galvanic cell (no continuous flow of electrons is possible). The tendency of losing electrons, however, still persists and electrons will be transferred as and when possible. Thus, a couple in isolation will maintain its reversible equilibrium. There is neither an outlet for the electrons if the forward oxidation reaction is to be maintained nor a source of supply of electrons if the backward reduction reaction is to be maintained.

Now if the Cu^{2+} ions are removed from the solution near the electrode, more copper would get dissolved and vice versa. Further, the removal of electrons from the metal strip will make the solution rich in Cu^{2+} ions. This would be counteracted by Cu^{2+} ions from the solution getting deposited after reduction as copper metal.

This tendency for a metal to get oxidized or conversion of its ions into metal by reduction is measured by the equilibrium constant, K

$$\text{Cu(s)} \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-}$$

$$\text{Therefore, } K = \frac{[\text{Cu}^{2+}(\text{aq})] [\text{e}^{-}]^2}{\text{Cu(s)}}$$

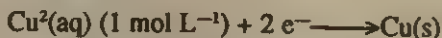
$$\text{or } [\text{Cu}^{2+}(\text{aq})] = K [\text{Cu(s)}] = K \text{ (since } [\text{Cu(s)}] = 1 \text{ and } [\text{e}^{-}]^2 = 1)$$

This tendency can also be expressed in terms of potential developed between the metal and its ions.

The potential difference at equilibrium depends on :

1. the metal and its ions
2. the concentration of the ions in the solution, and
3. temperature.

The potential difference between an electrode and the metal ions at 1 molar concentration (or unit activity) and at 298 K is called standard electrode potential (E°). The definition of a standard electrode potential can thus be



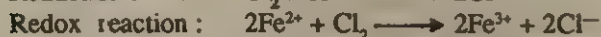
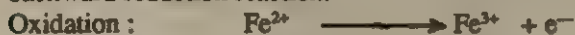
This is usually expressed as reduction reaction, hence, it is called standard reduction potential. By convention, standard electrode potential is taken just for a half-cell described by a reduction reaction.

We have already seen that a half-cell (or single electrode) by itself

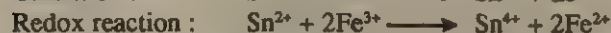
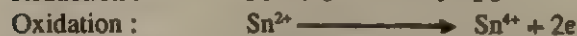
cannot cause movement of charges (flow of electricity). However, a mutual exchange of electrons and ions can take place if it is combined with another half-cell, giving rise to a redox reaction.

The forward oxidation reaction or backward reduction reaction of a half-cell depends on the nature of the second half-cell with which it is combined. This is illustrated by considering the reactions of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell (couple), together with (a) the Cl_2/Cl^- couple, and (b) the $\text{Sn}^{4+}/\text{Sn}^{2+}$ couple.

- (a) For the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple in the association of the couple Cl_2/Cl^- forward oxidation takes place and the Cl_2/Cl^- couple undergoes backward reduction reaction.



- (b) For the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple in the association of the $\text{Sn}^{4+}/\text{Sn}^{2+}$ couple, the backward reduction reaction takes place and the $\text{Sn}^{4+}/\text{Sn}^{2+}$ couple undergoes forward oxidation reaction.



The tendency to lose electrons by an element or ion (or conductor) is called **oxidation potential** and the tendency to accept electrons by an element or ion is called **reduction potential**.

Differences in electrode potential between pairs of electrodes can be determined with precision. Unfortunately the voltage produced by a single electrode in a cell cannot be measured directly. However, if an electrode with some arbitrary value is chosen as reference electrode (standard) then precise relative potentials can be determined for other electrodes by comparison with this reference.

10.4.2 Types of Single Electrodes

We cannot measure single electrode potential directly. However, it can be measured indirectly by coupling the electrode with a reference electrode. There are two types of reference electrodes :

1. Primary reference electrode
2. Secondary reference electrode

Hydrogen Electrode : Traditionally, the primary reference electrode with which all oxidation or reduction electrodes are compared is the standard hydrogen electrode (SHE) pictured in Fig. 10.10. It consists of platinum electrode coated with platinum black, immersed in a 1.0M H_3O^+ solution saturated with H_2 gas at 1 atm at 298 K. Platinum black catalyses the electrode reaction $2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g})$. Pure hydrogen (1 atm) is constantly bubbled around a platinum black electrode immersed in an acid solution of unit activity (1.0 M HCl) It has been

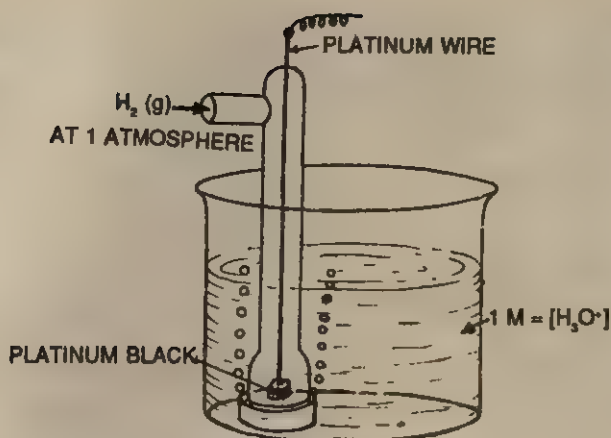


Fig. 10.10 Hydrogen electrode

arbitrarily assigned a potential of 0.00 V.

Thus, the standard hydrogen electrode often abbreviated as SHE, is

$\text{Pt(s)}, \text{H}_2(\text{g}, 1 \text{ atm}) \mid \text{H}^+(\text{a}=1 \text{ or } 1.0\text{M})$ as an anode, or

$\text{H}^+(\text{a}=1 \text{ or } 1 \text{ M}) \mid \text{H}_2(\text{g}, 1 \text{ atm}), \text{Pt(s)}$ as a cathode

The only practical difficulty in setting this electrode is the maintenance of 1 atm gas pressure. Several secondary electrodes, whose potentials are known on the hydrogen scale, are used in place of hydrogen electrode.

Calomel Electrode : It is a secondary reference electrode (Fig. 10.11)

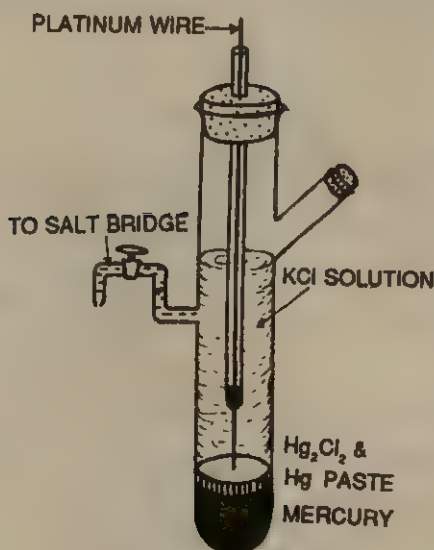
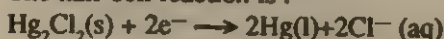


Fig. 10.11 Calomel electrode

This consists of mercury, solid mercurous chloride and a solution of potassium chloride (0.1M or 1M or saturated solution of KCl). The electrode is represented as : $\text{HgI}, \text{Hg}_2\text{Cl}_2(\text{s}) ; \text{KCl} (0.1 \text{ M or } 1.0 \text{ M or solid})$ as an anode or $\text{KCl}(0.1 \text{ M or } 1.0 \text{ M or solid})/\text{Hg}_2\text{Cl}_2(\text{s}), \text{Hg}(\text{l})$ as a cathode..

Mercury of a high degree of purity is used. Calomel electrode consists of a glass tube; mercury is placed at the bottom of it. Mercury is covered with a paste of mercurous chloride. A solution of KCl is filled in the tube above the paste. A platinum wire is fused in a glass tube to make electrical contact.

The half-cell reaction is :



The potentials of the calomel electrode determined using standard hydrogen electrode for different concentrations of potassium chloride at 298K are given below ;

For 0.1 M KCl solution $E^\circ = -0.3338$ volt

For 1M KCl solution $E^\circ = -0.2800$ volt

For saturated KCl solution $E^\circ = -0.2415$ volt

10.4.3 Experimental Measurement of Electrode Potential

The electrode potential of an electrode can be measured by comparing it to that of standard hydrogen electrode which has been given the potential of zero volt. For example, the standard electrode potential of zinc may be determined with the cell shown in Fig. 10.12. The cell notation is,



The electrode reactions are represented below :

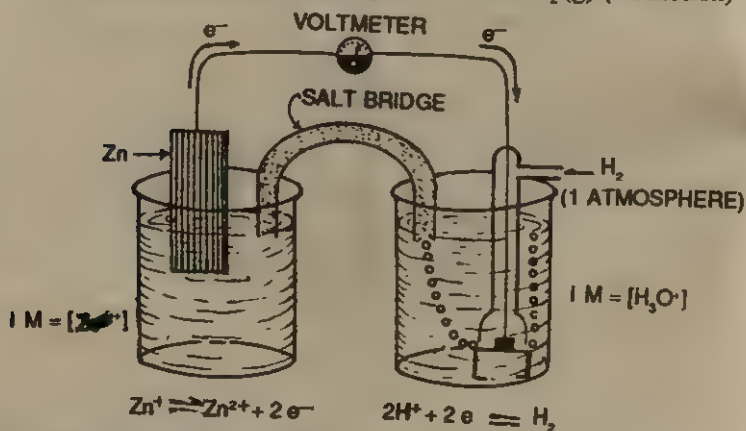
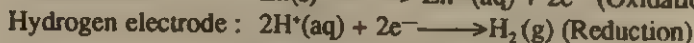
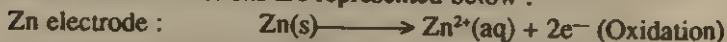


Fig. 10.12 : A Zn^{2+}/Zn couple in combination with SHE. Zn^{2+}/Zn acts as anode and SHE acts as cathode. The $E_{\text{Zn}^{2+}/\text{Zn}}^\circ$ is -ve

Oxidation takes place at the Zn electrode, and hence, cell potential is taken as electrode potential with negative sign. Thus, $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$ is —ve. However, if Cu electrode is connected with standard hydrogen electrode (Fig. 10.13) reduction takes place at the Cu electrode.

The cell notation is, $\text{Pt(s)} \mid \text{H}_2(\text{g}, 1 \text{ atm}) \mid \text{H}^+(\text{1M}) \parallel \text{Cu}^{2+}(\text{1M}) \mid \text{Cu(s)}$

The electrode reactions are represented below :

Hydrogen electrode : $\text{H}_2(\text{g}) \longrightarrow 2\text{H}^+ + 2\text{e}^-$ (Oxidation)

Copper electrode : $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu(s)}$ (Reduction)

The cell potential is taken as electrode potential of Cu electrode with positive sign. Thus, $E_{\text{Cu}^{2+}/\text{Cu}}$ is +ve.

The electrode potential can also be measured by combining it with calomel electrode and using the equation

$$E_{\text{cell}} = E_{\text{reduction}} - E_{\text{oxidation}}$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

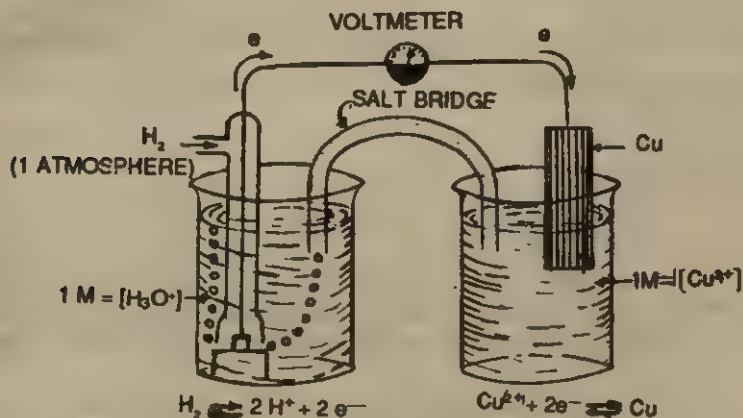


Fig. 10.13 : A Cu^{2+}/Cu couple in combination with SHE. Cu^{2+}/Cu acts as cathode and SHE acts as anode.

$$E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} \text{ is +ve.}$$

10.4.4 Measurement of EMF of a Cell using Potentiometer

When two electrodes in a galvanic cell are at different potentials, there is flow of electricity. This difference in potentials of two electrodes of a cell is called electromotive force (EMF).

The EMF of a cell can be measured with the help of a potentiometer. It consists of a wire AB of uniform diameter (Fig. 10.14). The storage battery C is connected to the two ends of a wire AB. The constant EMF of the storage battery must be larger than that of a cell under measurement. The cell whose EMF is to be measured is connected to A having the +ve pole in the same direction as the storage battery C

The other terminal of the cell is connected to a sliding contact O through a galvanometer, G. The sliding contact O is moved along the wire AB until no current flows through the galvanometer. This is called the null point. At this point the EMF of the cell is balanced by the potential difference between the points A and O.

$$\text{or } E_{\text{cell}} \propto AO \dots (1)$$

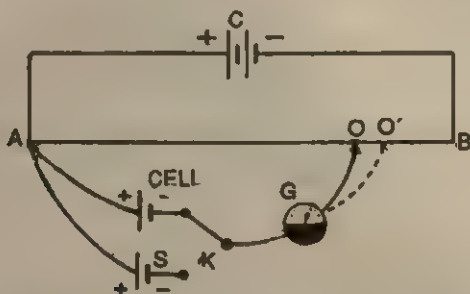


Fig.10.14: Measuring the EMF of a cell with the help of a potentiometer

The experiment is repeated with a standard cell, S whose EMF is known. Similarly,

$$E_s \propto AO \dots (2)$$

Thus, from (1) and (2)

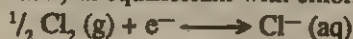
$$\frac{E_{\text{cell}}}{E_s} = \frac{AO}{AO}$$

Knowing E_s , one can calculate E_{cell} . Some standard half-cell electrode potentials for the reduction process in acid solution are given in Table 10.1.

The redox potential of metals with variable oxidation states can be measured if the redox potential for one ion in equilibrium with another of different charge can be determined. For example, iron exists in two states, i.e., Fe^{3+} and Fe^{2+} . The redox potential of the couple $\text{Fe}^{3+}/\text{Fe}^{2+}$ is estimated by measuring the EMF of the cell given with SHE (Pt wire being the inert electrode).



Similar to metals, the EMF for nonmetals (produce negative ions in aqueous solution) can be determined. For example, the E° of chlorine can be determined by employing an electrode which contains chlorine gas (1 atm) in equilibrium with chloride solution, (1M),



The E° values for a number of non-metals, have been listed in Table 10.1.

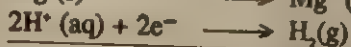
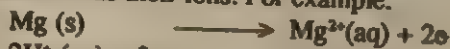
TABLE 10.1 Some standard electrode (or reduction) potential at 298K in acid solution (electrochemical series)

Couple (Electrode)	Half-reaction	E° (Volts)
Li ⁺ /Li	Li ⁺ + e ⁻ → Li	-3.05
M ⁺ /M (M=K, Rb or Cs)	M ⁺ + e ⁻ → M	-2.93
Ba ²⁺ /Ba	Ba ²⁺ + 2e ⁻ → Ba	-2.90
Sr ²⁺ /Sr	Sr ²⁺ + 2e ⁻ → Sr	-2.89
Ca ²⁺ /Ca	Ca ²⁺ + 2e ⁻ → Ca	-2.76
Na ⁺ /Na	Na ⁺ + e ⁻ → Na	-2.71
Mg ²⁺ /Mg	Mg ²⁺ + 2e ⁻ → Mg	-2.38
Al ³⁺ /Al	Al ³⁺ + 3e ⁻ → Al	-1.67
Zn ²⁺ /Zn	Zn ²⁺ + 2e ⁻ → Zn	-0.76
Cr ³⁺ /Cr	Cr ³⁺ + 3e ⁻ → Cr	-0.74
CO ₂ /H ₂ C ₂ O ₄	2CO ₂ + 2H ⁺ + 2e ⁻ → H ₂ C ₂ O ₄	-0.49
Fe ²⁺ /Fe	Fe ³⁺ + 2e ⁻ → Fe	-0.44
Cr ³⁺ /Cr ²⁺	Cr ³⁺ + e ⁻ → Cr ²⁺	-0.41
Cd ²⁺ /Cd	Cd ²⁺ + 2e ⁻ → Cd	-0.40
SO ₄ ²⁻ /Pb, PbSO ₄	PbSO ₄ + 2e ⁻ → Pb + SO ₄ ²⁻	-0.31
Co ³⁺ /Co	Co ³⁺ + 2e ⁻ → Co	-0.28
Ni ²⁺ /Ni	Ni ²⁺ + 2e ⁻ → Ni	-0.25
Sn ²⁺ /Sn	Sn ²⁺ + 2e ⁻ → Sn	-0.14
Pb ²⁺ /Pb	Pb ²⁺ + 2e ⁻ → Pb	-0.13
H ⁺ /½H ₂ , Pt	H ⁺ + e ⁻ → ½H ₂	-0.00 (by definition)
Sn ⁴⁺ /Sn ²⁺	Sn ⁴⁺ + 2e ⁻ → Sn ²⁺	0.15
Cu ²⁺ /Cu ⁺	Cu ²⁺ + e ⁻ → Cu ⁺	0.15
Cu ²⁺ /Cu	Cu ²⁺ + 2e ⁻ → Cu	0.34
Cu ⁺ /Cu	Cu ⁺ + e ⁻ → Cu	0.52
½I ₂ /I ⁻	½I ₂ + e ⁻ → I ⁻	0.54
Fe ³⁺ /Fe ²⁺	Fe ³⁺ + e ⁻ → Fe ²⁺	0.77
Hg ₂ ²⁺ /Hg	½Hg ₂ ²⁺ + e ⁻ → Hg	0.80
Ag ⁺ /Ag	Ag ⁺ + e ⁻ → Ag	0.80
Hg ₂ ²⁺ /Hg	Hg ₂ ²⁺ + 2e ⁻ → Hg	0.85
½Br ₂ /Br ⁻	½Br ₂ + e ⁻ → Br ⁻	1.09
½Cr ₂ O ₇ ²⁻ /Cr ³⁺	½Cr ₂ O ₇ ²⁻ + 7H ⁺ + 3e ⁻ → Cr ³⁺ + ½H ₂ O	1.33
½Cl ₂ /Cl ⁻	½Cl ₂ + e ⁻ → Cl ⁻	1.36
O ₂ /O ₂	O ₂ + 2H ⁺ + 2e ⁻ → O ₂ + H ₂ O	2.07
½F ₂ /F ⁻	½F ₂ + e ⁻ → F ⁻	2.87
½F ₂ /HF	½F ₂ + H ⁺ + e ⁻ → HF	3.06

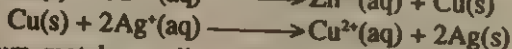
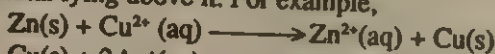
10.4.5 Electrochemical Series

Half-cell potential or electrode potential predicts the relative ease with which the various species of metals and ions constituting the half-cells may be oxidized or reduced. The Table 10.1 has been arranged with the strongest oxidizing agent F₂ at the bottom and the weakest oxidizing agent, Li at the top. The strength of an oxidizing agent depends on the ease with which the compound will accept electrons. Thus, fluorine has the strongest tendency to accept electrons. Lithium has the least tendency to accept electrons. High negative reduction potential for

the lithium electrode supports its least tendency of accepting electrons, i.e., Li^+ ions do not get reduced easily. It also predicts that Li^+ is easily oxidized than H^+ ion. Thus, lithium metal displaces H_2 from a solution having H^+ ions. Hence, all metals lying above hydrogen in the electrochemical series displace H_2 gas from a dilute acidic solution. Metals pass into solution as their ions. For example,



In Table 10.1, the most active metal has been put at the top. Metals with highest -ve electrode reduction potential can displace other metals from their salts. In other words, any metal will reduce the ions of any metal lying below it and, conversely, its own ions are reduced by any metal lying above it. For example,



Lithium metal can displace all other metals from their salt solutions. Half-cell potentials can be combined to determine the potentials for various galvanic cells.

10.4.6 Applications of Electrochemical Series

1. E° values from Table 10.1 predicts relative strengths of oxidizing and reducing agents. We can also predict whether a given metal would liberate hydrogen or not form an acid. This is discussed in detail above.

2. Calculation of standard EMF of a Galvanic Cell (E°_{cell}): The standard EMF of a cell (E°_{cell}) is equal to

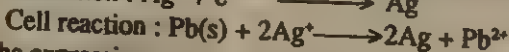
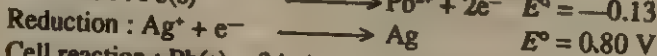
$$E^\circ_{\text{cell}} = E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

where E°_{right} is the standard reduction potential of the electrode on the right and E°_{left} is the standard reduction potential of the electrode on the left.

1. Spontaneity of redox reactions: If E°_{cell} of a cell, as calculated above, is +ve and the half-cell reaction taking place at the left electrode is written as an oxidation reaction and the half-cell reaction taking place at the right electrode is written as a reduction reaction, taking cell reaction as the sum of these two, it would be spontaneous.

Exercise 10.1 What is the cell reaction and what is the emf at 298K of the cell, $\text{Pb} \mid \text{Pb}^{2+} (\text{a} = 1) \mid \text{Ag}^+ (\text{a} = 1) \mid \text{Ag}$.

Solution: The cell reaction is,



in the expression

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$= 0.80 - (-0.13)$$

$$E^\circ_{\text{cell}} = 0.80 + 0.13 = 0.93 \text{ V}$$

The value indicates that lead will be the anode and the silver will be the cathode. The reaction is spontaneous.

Exercise 10.2 : (a) Calculate the standard cell potential for the cell $\text{Zn}; \text{Zn}^{2+} (1\text{M}) \parallel \text{Cd}^{2+} (1\text{M}) ; \text{Cd}$, (b) Write the cell reaction for this cell. (c) Is the cell reaction spontaneous or not ?

Solution : (a) From the table of standard electrode potentials, the reduction potential for the couple Zn^{2+}/Zn is, $E^\circ = -0.40 \text{ V}$. Putting these values in the expression,

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= -0.40 - (-0.76) \\ &= -0.40 + 0.76 = 0.36 \text{ V} \end{aligned}$$

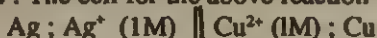
(b) The cell reaction for the cell is $\text{Zn} + \text{Cd}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cd}$

(c) Since the emf of the cell is positive, the reaction written is spontaneous. Zinc loses electrons and cadmium ions gain them.

Exercise 10.3 : Will Ag reduce copper ion at 298K according to the reaction ?



Solution : The cell for the above reaction is,



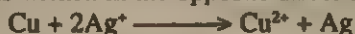
For the couple, Ag^+/Ag the reduction potential, $E^\circ = +0.80 \text{ V}$

For the couple Cu^{2+}/Cu the reduction potential, $E^\circ = +0.34 \text{ V}$

Putting the values in the expression,

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= 0.34 - (+0.80) \\ &= 0.34 - 0.80 = -0.46 \text{ V} \end{aligned}$$

The negative value of E°_{cell} indicates that the reaction will not go spontaneously, i.e., silver will not reduce Cu^{2+} ion. However, if the reaction is written in the opposite direction, i.e.,

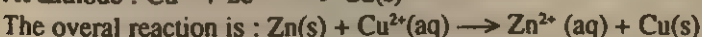
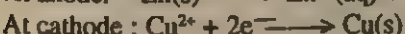
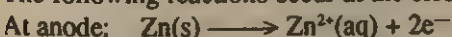


and the electrode on which the oxidation reaction $\text{Cu} \longrightarrow \text{Cu}^{2+} + 2\text{e}^-$ occurs is placed on the left, the cell is written as,



10.5 OTHER VOLTAIC CELLS (COMMERCIAL CELLS)

(i) **Daniel Cell (Fig. 10.15) :** It consists of a copper vessel which has been divided into two parts by a circular porous pot. Anode made of zinc is immersed in ZnSO_4 solution contained in a porous pot. The pot is surrounded by copper sulphate solution. Copper vessel works as cathode. The following reactions occur at the electrodes :



The emf of the Daniel cell in the beginning is 1.1 volt and this decreases gradually. The emf of the cell depends upon the intensity of the chemi-

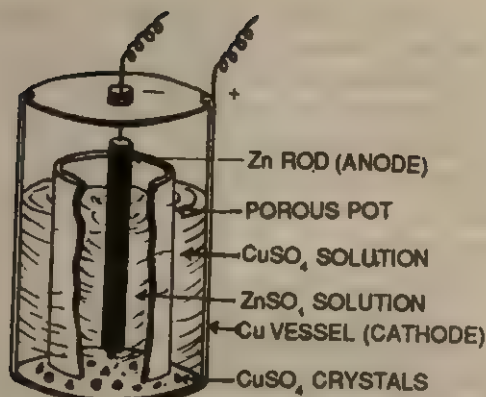


Fig. 10.15 : Daniel cell

cal reaction taking place inside the cell. Intensity of the chemical reaction decreases gradually and hence, emf of the cell decreases gradually. The porous partition allows the migration of ions when the cell is in use. It decreases the diffusion of ions to a large extent when the cell is not in use. This is a practical but less efficient way of preventing mixing of the two electrolytes.

(ii) Dry Cell (Leclanche cell) (Fig. 10.16): The vessel made of zinc

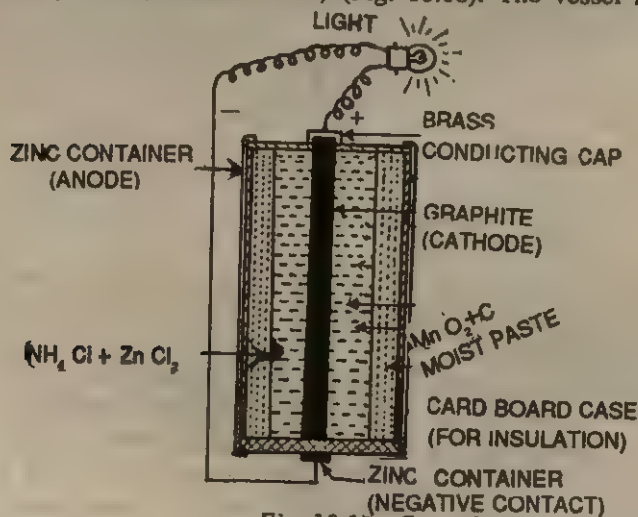
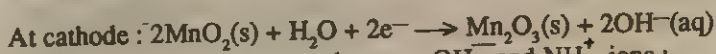


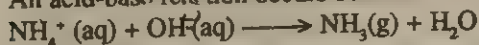
Fig. 10.16 : Dry cell

metal serves as an anode, the graphite rod with a brass cap passing through the cell is the cathode. The space between the electrodes is filled with a moist paste of manganese dioxide, carbon black, zinc chloride and ammonium chloride. Its voltage is 1.25 V to 1.5V. The following reactions take place at electrodes when the cell is in use :

At anode : $\text{Zn(s)} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$. The cathode reaction is very complex. It seems that MnO_2 is reduced; a plausible reduction reaction is :

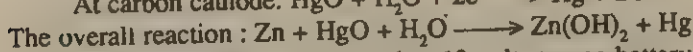
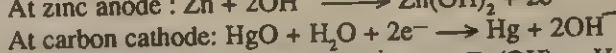
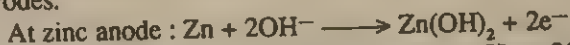


An acid-base reaction occurs between OH^- and NH_4^+ ions :



At times, when a large current is drawn, ammonia produced by the reaction forms an insulating gaseous layer around cathode (carbon) and disrupts the electric current. In the normal course this does not happen as Zn^{2+} ions migrate to the cathode and react with ammonia molecules to form complex ions, such as $[\text{Zn}(\text{NH}_3)_4]^{2+}$. A so called 'dead' dry cell can sometimes be put to use again by careful heating which increases the rate of diffusion of Zn^{2+} ions across the cell. During use the zinc casing gets consumed and holes start appearing. These holes are responsible for leakages. Leak proof dry cells have been provided with an extra casing surrounding the zinc vessel.

A cell (EMF = 1.35V), developed for hearing aids and other small electrical devices, consists of a moist paste of HgO and KOH between the two electrodes. A lining of porous paper is interposed between zinc anode and the moist paste. The following reactions take place at the two electrodes.



(iii) **Lead Storage Battery** : The 6 or 12 volt storage battery commonly employed in automobiles consists of 3 or 6 voltaic cells (Fig. 10.17) in

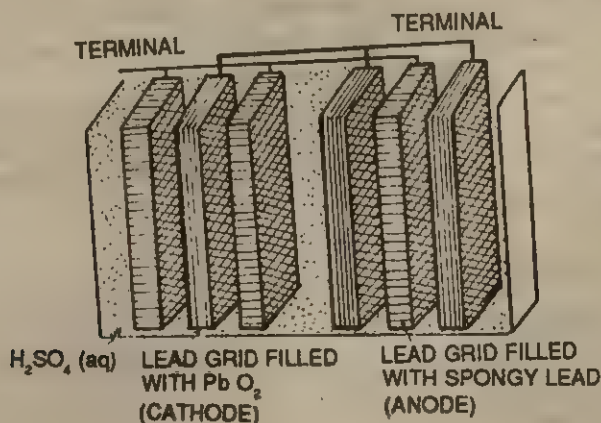
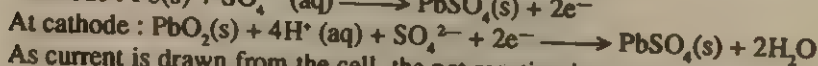
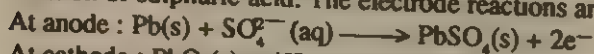
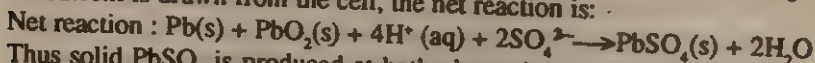


Fig. 10.17 : Lead storage battery

series. The multiple lead cathode of a fully charged cell is a group of plates filled with lead dioxide. The anode also consists of a group of lead plates, the grids of which are packed with spongy grey lead. These two series of plates are arranged alternately and are immersed in a water solution of sulphuric acid. The electrode reactions are :



As current is drawn from the cell, the net reaction is :



Thus solid PbSO_4 is produced at both electrodes, as the cell discharges.

Simultaneously H^+ and SO_4^{2-} (or HSO_4^-) are removed from the solution

Solid PbSO_4 produced during reactions slowly deposit on the plates,

partially covering and replacing the lead and lead dioxide. Concentration

of H_2SO_4 decreases as the cell discharges. Low density of the electrolyte

shows low concentration. The electrode reactions can be reversed by

passing an electric current through it, and thus, the battery can be re-

charged. This causes all the reactions to reverse as the cell be-

comes an electrolytic cell, converting PbSO_4 to Pb and to PbO_2 at the

respective electrodes.

10.6 DEPENDENCE OF EMF ON CONCENTRATION AND TEMPERATURE

10.6.1 The Electrode Potential

We have stated earlier that the value of the measured electrode potential depends on the concentration of all substances involved in the reaction.

The increase in ion concentration will tend to shift the equilibrium in the reverse direction thereby decreasing the tendency for metal to lose electrons and a decrease in metal ion concentration will increase the electrode potential. Electrode potential also depends upon the material of the electrode.

The equation that relates the measured electrode potential, E to the concentrations of the reactants and the temperature is called the Nernst's Equation. The potential E of a cell is given by the expression,

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

In this equation Q is the reaction quotient i.e., an expression that has the same form as the expression for the equilibrium concentrations. In this equation, E is the electrode potential, E° is the standard electrode potential; F is the farady (96500 coulombs); R is a gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$); T is Kelvin temperature; n is the number of electrons involved in the change in oxidation state, (or n is the number

of moles of electrons transferred in the reaction); \ln represents natural logarithm (logarithm to the base e not to the base 10). The relationship between $\log x$ and $\ln x$ is $\ln x = 2.303 \log x$.

Substituting the values of the constants, at 298K,

$$\frac{RT}{F} = \frac{8.314 \text{ JK}^{-1} (298 \text{ K})}{96500 \text{ C mol}^{-1}} = 0.0257 \text{ V} = 0.0257 \text{ J C}^{-1}$$

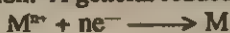
Thus at 298K the Nernst equation becomes,

$$E = E^\circ - \frac{0.0257}{n} \log Q$$

On converting natural logarithm to common logarithm,

$$E = E^\circ - \frac{0.0592}{n} \log Q$$

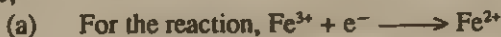
Using this equation, we can calculate the potential of a cell if we know the concentration of the reactants and the standard cell potential, E° . For reduction electrode potentials, the half-cell is written in terms of reduction reaction. A general reduction process is,



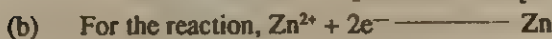
The Nernst equation for the reduction process is written as,

$$E = E^\circ - \frac{0.0592}{n} \log \frac{[M]}{[M^{n+}]}$$

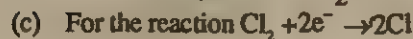
Concentrations are measured in moles per litre. For accurate results ionic activities are used instead of ionic concentrations. The concentrations of pure solids or liquids are set at unity. For a gas, the concentration is equal to the pressure of the gas in atmosphere. For example,



$$E = E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} - \frac{0.0592}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$



$$E = E^\circ_{\text{Zn}^{2+}/\text{Zn}} - \frac{0.0592}{2} \log \frac{1}{[\text{Zn}^{2+}]}$$



$$E = E^\circ_{\frac{1}{2} \text{Cl}_2/\text{Cl}^-} - \frac{0.0592}{2} \log \frac{[\text{Cl}^-]^2}{[\text{Cl}_2]}$$

Exercise 10.4 : Calculate the half-cell potential at 298K for the reduction from H^+ at $1.0 \times 10^{-7} \text{ M}$ to H_2 at 1.0 atm.

Solution : $2\text{H}^+ (1 \text{ M}) + 2e^- \longrightarrow \text{H}_2 (1 \text{ atm}); E^\circ = 0.00 \text{ V}$

According to Nernst's equation,

$$E = E^\circ - \frac{0.0592}{n} \log \frac{[\text{H}_2(\text{p})]}{[\text{H}^+]^2} = 0.00 - \frac{0.0592}{2} \log \frac{1.0}{[1.0 \times 10^{-7}]^2}$$

$$= 0.00 - \frac{0.0592}{2} (+14)$$

$$E = -0.41 \text{ V}$$

Therefore, $2\text{H}^+ (1.0 \times 10^{-7}\text{M}) + 2\text{e}^- \longrightarrow \text{H}_2 (1.0 \text{ atm}); E = 0.41 \text{ V}$

Exercise 10.5 : Calculate the half-cell potential at 298K for the reaction $\text{Zn}^{2+} (\text{aq}) + 2\text{e}^- \longrightarrow \text{Zn}(\text{s})$; if Zn^{2+} is 5.0 M and $E^\circ = -0.76\text{V}$.

Solution : According to Nernst's equation

$$E = E^\circ - \frac{0.0592}{2} \log \frac{[\text{Zn}]}{[\text{Zn}^{2+}]}$$

$$= -0.76 - \frac{0.0592}{5.0} \log \frac{1}{5.0}$$

$$= -0.76 - 0.0296 (-0.70)$$

$$= -0.76 + 0.02 = -0.74 \text{ V}$$

10.6.2 The Cell Potential

Let us consider the Daniel cell,



The electrode potentials of the two half-cells are,

$$E_{\text{right}} = E^\circ_{\text{right}} + \frac{RT}{2F} \ln [\text{Cu}^{2+}(\text{aq})]$$

$$E_{\text{left}} = E^\circ_{\text{left}} + \frac{RT}{2F} \ln [\text{Zn}^{2+}(\text{aq})]$$

(In the Daniel cell the oxidation state of both Zn and Cu is 2) Now the EMF of the cell is equal to the EMF of the right hand electrode minus the EMF of the left-hand electrode, i.e.,

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

$$E_{\text{cell}} = E^\circ_{\text{right}} + \frac{RT}{2F} \ln [\text{Cu}^{2+}(\text{aq})] - [E^\circ_{\text{left}} + \frac{RT}{2F} \ln [\text{Zn}^{2+}(\text{aq})]]$$

$$= (E^\circ_{\text{right}} - E^\circ_{\text{left}}) + \frac{RT}{2F} \ln \frac{[\text{Cu}^{2+}(\text{aq})]}{[\text{Zn}^{2+}(\text{aq})]}$$

Now on substituting the value of standard electrode potentials for the two couples, other constants and converting natural logarithm to the base 10 at 298K,

$$E_{\text{cell}} = 0.34 - (-0.76) + \frac{2.303RT}{2F} \log \frac{[\text{Cu}^{2+}(\text{aq})]}{[\text{Zn}^{2+}(\text{aq})]} \text{ or}$$

$$= 1.1 + \frac{0.0592}{2} \log \frac{[\text{Cu}^{2+}(\text{aq})]}{[\text{Zn}^{2+}(\text{aq})]}$$

This equation can be used to calculate the EMF of the cell provided we know the concentration of the two metal ions employed in the cell, e.g., if the concentration of copper sulphate solution is 0.01M and that of ZnSO_4 is 0.1M at a temperature 298K,

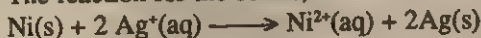
$$E_{\text{cell}} = 1.1 + \frac{0.0592}{2} \log \frac{[0.01]}{[0.1]}$$

$$= 1.1 + 0.0296 \log \frac{1}{10}$$

$$= 1.1 - 0.0296 = 1.07 \text{ V}$$

Now let us consider another cell which involves the metals ions at different oxidation states, e.g., $\text{Ni(s)} \mid \text{Ni}^{2+}(\text{aq}) \parallel \text{Ag}^+(\text{aq}) \mid \text{Ag(s)}$

The reaction for the cell is,



The electrode potential of silver and nickel half-cells are as given below :

$$E_{\text{Ag}} = E^\circ_{\text{Ag}^+/\text{Ag}} + \frac{RT}{F} \ln [\text{Ag}^+(\text{aq})] \text{ (since } n = 1)$$

$$\text{or } E_{\text{Ag}} = E^\circ_{\text{Ag}^+/\text{Ag}} + \frac{RT}{2F} \ln [\text{Ag}^+(\text{aq})]^2$$

$$\text{and } E_{\text{Ni}} = E^\circ_{\text{Ni}^{2+}/\text{Ni}} + \frac{RT}{2F} \ln [\text{Ni}^{2+}(\text{aq})] \text{ (since } n = 2)$$

While calculating the EMF of such a cell and writing the electrode potential for the couple $\text{Ag}^+(\text{aq})/\text{Ag(s)}$ one has to be careful in substituting the value of concentration and valence (number of electrons involved in the change in oxidation state). Here, one Ni atom releases two electrons in the course of reaction, and hence, reduction reaction of silver ion, i.e., $\text{Ag}^+(\text{aq}) + e^- \longrightarrow \text{Ag(s)}$ has to be multiplied by numeral 2 to balance the equation. But the value of E°_{Ag} remains unaltered.

Now the EMF of the cell will be,

$$E = E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

By making substitutions, according to Daniel cell we get,

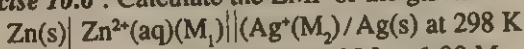
$$E = E^\circ_{\text{Ag}} - E^\circ_{\text{Ni}} + \frac{RT}{2F} \ln \frac{[\text{Ag}^+(\text{aq})]^2}{[\text{Ni}^{2+}(\text{aq})]}$$

By substituting the E° for the two electrodes and converting natural logarithm to common logarithms we get,

$$\begin{aligned} E &= 0.80 + (-0.25) + 2.303 \frac{RT}{2F} \log \frac{[\text{Ag}^+(\text{aq})]^2}{[\text{Ni}^{2+}(\text{aq})]} \\ &= 1.05 + 2.303 \frac{RT}{2F} \log \frac{[\text{Ag}^+(\text{aq})]^2}{[\text{Ni}^{2+}(\text{aq})]} \end{aligned}$$

Thus, the expression for EMF for a cell can be arrived at depending upon the reactions taking place in the two half cells and the concentrations of the reactants employed in the cell.

Exercise 10.6 : Calculate the EMF of the galvanic cell



When 1 $M_1 = 1.00 \text{ M}$ and $M_2 = 1.00 \text{ M}$

2 $M_1 = 0.100 \text{ M}$ and $M_2 = 0.01 \text{ M}$

3 $M_1 = 0.012 \text{ M}$ and $M_2 = 0.200 \text{ M}$

Solution : 1. When the concentration of both the metal ions is the standard one, i.e., 1M, then the cell potential is equal to the standard cell potential. The net reaction for the cell is,

$\text{Zn(s)} + 2 \text{Ag}^+(\text{aq}) \longrightarrow 2 \text{Ag(s)} + \text{Zn}^{2+}(\text{aq})$ and therefore, the Q , the reaction quotient is, $[\text{Zn}^{2+}]/[\text{Ag}^+]^2$

Now the Nernst equation is,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log Q$$

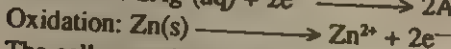
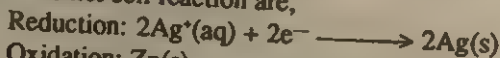
$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2} \log \frac{1}{1}$$

$$\begin{aligned} E_{\text{cell}} - E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{Ag}^+/\text{Ag}} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} \\ &= 0.80 \text{ V} - (-0.763 \text{ V}) \\ &= 1.56 \text{ V} \end{aligned}$$

2. When $\text{Zn}^{2+} = 0.100 \text{ M}$ and $[\text{Ag}^+] = 0.01 \text{ M}$

$$Q = \frac{0.1}{[0.01]^2} = \frac{1.00 \times 10^{-1}}{1.0 \times 10^{-4}} = 1.0 \times 10^3 = \log Q = 3.00$$

For this reaction $n = 2$ because the two half reactions that combine to give the net cell reaction are,



The cell potential from the Nernst equation will be :

$$\begin{aligned} E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \frac{0.0592}{2} \log Q \\ &= 1.56 - \frac{0.0592}{2} \log (1.0 \times 10^3) \\ &= 1.56 - 0.089 = 1.471 \text{ V} \end{aligned}$$

This may be noted that when $Q = [\text{Zn}^{2+}]/[\text{Ag}^+]^2$ is greater than 1, the cell potential is less than the standard cell potential.

3. When $[\text{Zn}^{2+}] = 1.2 \times 10^{-2} \text{ M}$ and $[\text{Ag}^+] = 2.00 \times 10^{-1} \text{ M}$

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = \frac{1.2 \times 10^{-2}}{4.00 \times 10^{-1}} = 0.30 = 3.0 \times 10^{-1}$$

Therefore $\log Q = -1 \log 10 + \log 3 = -1 + 0.48 = -0.52$

Now the cell potential, from the Nernst equation will be :

$$\begin{aligned} E_{\text{cell}} &= 1.56 - \frac{0.0592}{2} \times (-0.52) \\ &= 1.56 + 0.015 = 1.575 \text{ V} \end{aligned}$$

This may again be noted that when $[\text{Zn}^{2+}]/[\text{Ag}^+]^2$ is less than 1, the cell potential is greater than the standard cell potential.

10.6.3 Electrical Units

It will not be out of place to introduce the students to the electrical units as some units have already been used.

Coulomb (C) : It is the quantity of electricity which deposits 0.001118g of silver on a silver cathode from a silver salt solution.

$$\begin{aligned} 1 \text{ coulomb} &= 3 \times 10^9 \text{ esu} \\ 1 \text{ faraday} &= 96500 \text{ coulombs} \end{aligned}$$

= charge carried by one mole of electrons

Ampere (A): It measures the strength of an electric current. When one coulomb of electricity is passed through a conductor for one second, the

quantity of electrical current is one ampere. Thus,

$$1 \text{ coulomb} = 1 \text{ ampere} \times 1 \text{ second}$$

Volt (V) : It measures the difference in potential energy of electrons at two points. Potential difference is measured in units of work. Thus, a volt is a joule per coulomb, or it is the difference in potential energy of 1 joule for 6.02×10^{23} electrons

$$1 \text{ joule} = 1 \text{ coulomb} \times 1 \text{ volt}$$

Ohm (Ω) : It measures the resistance to the flow of electric current through a conductor.

$$1 \text{ volt} = 1 \text{ ohm} \times 1 \text{ ampere}$$

Watt (W) : It is a measure of power. One watt is equivalent to one joule per second ($W = Js^{-1}$).

$$\begin{aligned} \text{Watts} &= \frac{\text{joules}}{\text{seconds}} = \frac{\text{coulombs} \times \text{volts}}{\text{seconds}} \\ &= \text{amperes} \times \text{volts} \end{aligned}$$

$$\text{and } \text{joules} = \text{watts} \times \text{seconds}$$

10.6.4 Electrical Work and Free Energy Change

Electrical work is performed when a reaction takes place in a galvanic cell. The amount of work is given by the expression,

$$-\Delta G = +nF E_{\text{cell}}$$

Where n is the number of moles of electrons transferred between the electrodes, F is the faraday constant which gives the charge associated with 1 mole of electrons; therefore, it will be equal to the product of charge on an electron (1.602×10^{-19} coulomb) and Avogadro's number (6.023×10^{23} electrons per mole of electrons). That is, $(1.602 \times 10^{-19} \text{ C electron}) \times (6.023 \times 10^{23} \text{ electrons per mole of electrons}) = 96500 \text{ coulombs per mole of electrons or } 96500 \text{ C/mol } e^-$. If the reactants and products are in their standard states, then

$$-\Delta G^\circ = nF E^\circ_{\text{cell}}$$

Now the Nernst equation in terms of free energy takes the form, i.e.,

$$E = E^\circ - \frac{2.303 RT}{nF} \log Q$$

Substituting for E and E° from the free energy expressions, we get,

$$-\Delta \frac{G}{nF} = \Delta \frac{G^\circ}{nF} - \frac{2.303 RT}{nF} \log Q$$

$$\text{or/also } -\Delta \frac{G}{nF} = \Delta \frac{G^\circ}{nF} + \frac{2.303 RT}{nF} \log Q$$

$$\Delta G = \Delta G^\circ + 2.303 RT \log Q$$

Equilibrium constant : A galvanic cell can produce electricity only when the cell reaction is not at equilibrium, that is, when reaction quotient, Q K_{eq}

When the system is at equilibrium, two conditions must hold, i.e., $Q = K_{\text{eq}}$ and $E_{\text{cell}} = 0$

Now the Nernst equation for a system at equilibrium at 298K will be,

$$0 = E^{\circ}_{\text{cell}} - \frac{2.303 RT}{nF} \log K_{\text{eq}}$$

$$\text{or } E^{\circ}_{\text{cell}} = \frac{2.303 RT}{nF} \log K_{\text{eq}}$$

$$\log K_{\text{eq}} = \frac{E^{\circ}_{\text{cell}} nF}{2.303 RT}$$

This equation is useful to calculate the equilibrium constant for any oxidation reduction reaction in aqueous solution from the standard cell potential.

10.7 ELECTROLYSIS

Electric current brings about oxidation and reduction reactions and the process which takes place within the cell is known as electrolysis. It means electricity has been utilized to perform some chemical work, i.e., some chemical change. Humphry Davy, an English scientist, isolated sodium, potassium, magnesium and calcium by passing an electric current through molten hydroxides of these metals. The cell in which such electrolysis are performed is known as electrolytic cell.

Thus, there are two kinds of electrochemical equipment. In the first (Fig. 10.18) an external voltage is used to derive a current through a solution of electrolyte. Through the cathode (negative electrode) electrons enter the solution and a reduction reaction takes place. At the anode (positive electrode) an oxidation reaction takes place and electrons leave the solution. The sum of the anode and cathode reactions is a decomposition process for the electrolyte in solution. The driving force for this decomposition reaction is supplied by the external voltage source.

In the second type of experiment, which we have already discussed in the earlier sections, chemical reactions at the electrodes force electrons to flow through external circuit, oxidation taking place at the anode and reduction taking place at the cathode.

In the electrolysis of $\text{CuCl}_2(\text{aq})$ copper deposits at the cathode because the Cu^{2+} ions attract electrons and are reduced.

At the cathode : $\text{Cu}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Cu}(\text{s})$ Reduction

Simultaneously, the chloride ions move towards anode where two chloride ions lose two electrons, and thereby, oxidized forming a molecule of $\text{Cl}_2(\text{g})$

At the anode: $2\text{Cl}^- \longrightarrow \text{Cl}_2(\text{g}) + 2e^-$ (Oxidation)

The net equation of an oxidation-reduction process occurring in an electrolytic cell is obtained by adding the reactions :

Cathodic reaction : $\text{Cu}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Cu}(\text{s})$

Anodic reaction : $2\text{Cl}^- \longrightarrow \text{Cl}_2(\text{g}) + 2e^-$

The net equation : $\text{Cu}^{2+}(\text{aq}) + 2\text{Cl}^- \longrightarrow \text{Cl}_2(\text{g}) + \text{Cu}(\text{s})$

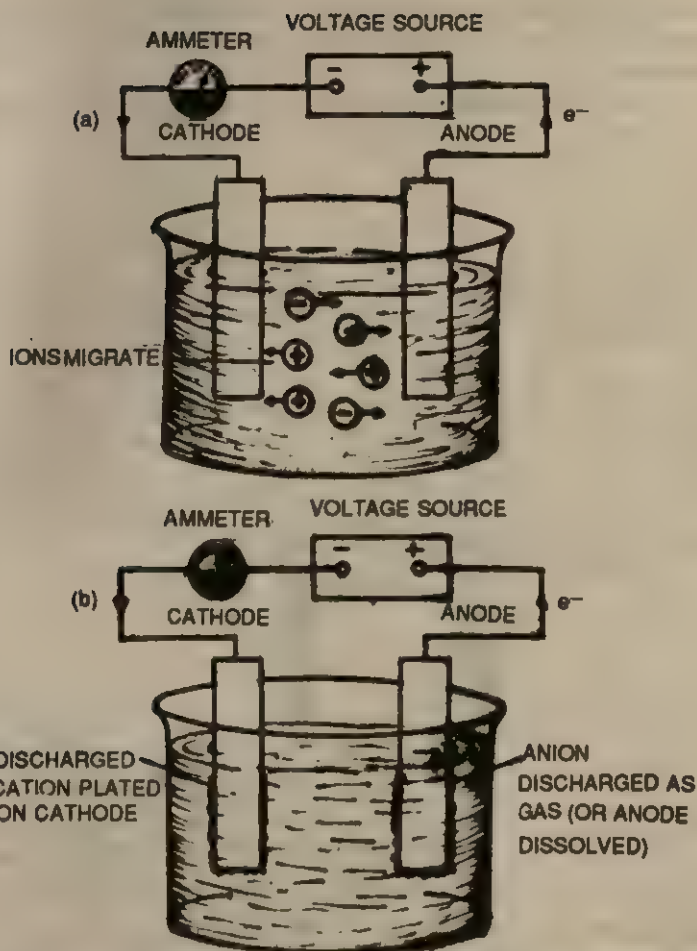
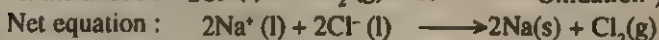
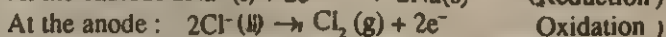


Fig. 10.18 : Electrolytic cell : (a) An external voltage source drives electrons through the solution producing oxidation at the anode and reduction at the cathode. (b) electrolysis of the electrolyte solution.

In the electrolysis of molten sodium chloride, sodium metal and chlorine gas are produced.



10.7.1 Electrolysis of Acidified Water

Pure water is a poor conductor of electricity. When electric current is passed through pure water no decomposition takes place. This can be

confirmed by inserting a bulb in the circuit of the electrolytic cell. Conduction through water will be signalled by the glowing bulb in the circuit path.

Now set up an apparatus as shown in Fig. 10.19 and take the water

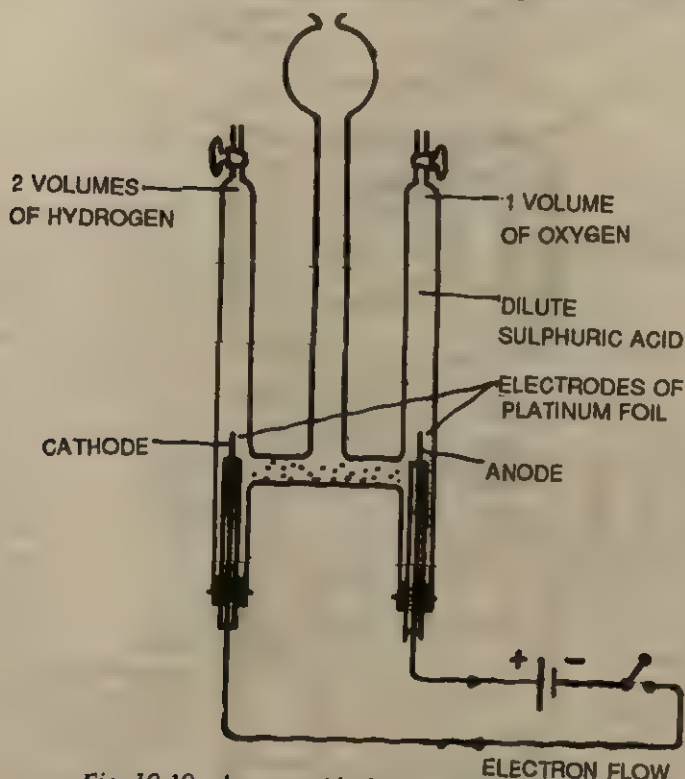
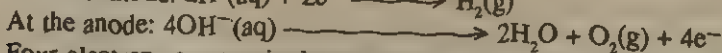
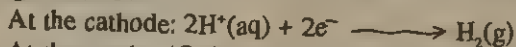


Fig. 10.19 : An assembly for electrolydising acidified water

acidified with dilute H_2SO_4 in the cell. Now on passing the current, two volumes of hydrogen are formed for every one volume of oxygen. The positively charged hydrogen ions are attracted by the negatively charged cathode, and start moving in that direction. The negatively charged hydroxide ions are attracted by the positively charged anode, and start moving towards it.



Four electrons are required to produce one molecule of oxygen by discharge of four OH^- ions. This same quantity of electricity is involved in the production of two moles of hydrogen by the discharge of four H^+ ions. Therefore, two molecules of hydrogen are produced for every molecule of oxygen and this is in agreement with the Avogadro's law, i.e., two volumes of hydrogen are produced for every volume of oxygen.

Along with OH^- ions, sulphate ions also move towards the anode thereby decreasing the concentration of H_2SO_4 in the neighbourhood of the cathode. Sulphate ions accumulate at the anode. The discharge of OH^- ion at the anode causes more water to ionize resulting in an increase of H^+ ion concentration. It means that there is an increase of H_2SO_4 concentration in the neighbourhood of the anode. Thus, the total amount of sulphuric acid in the solution remains constant, and the hydrogen and oxygen being produced come from water only.

The extent of a chemical reaction will depend upon the amount of electric charge transported through the cell. The answer to this lies with the laws of electrolysis advanced by Michael Faraday.

10.7.2 Laws of Electrolysis

In 1834 Michael Faraday, deduced the following two laws :

First Law : The amount of any substance that is deposited or liberated at any electrode is directly proportional to the quantity of electricity passed through the electrolyte. Mathematically,

$$W \propto Q \dots (10.1)$$

where W is the mass in g of a substance deposited and Q is the quantity of electricity in coulombs.

If 'I' ampere of current is flowing through the electrolyte in time, t seconds then,

$$Q = I \times t, \dots (10.2) \quad W \propto I \times t, \dots (10.3)$$

$$= Z \times I \times t \dots (10.4)$$

where Z is a constant of proportionality and is called the electrochemical equivalent.

when $I = 1$ and $t = 1$ second, $W = Z$

From this it follows that electrochemical equivalent is the amount of a substance in g deposited by 1 ampere current passing for 1 second.

Second Law : When the same quantity of electricity is passed through different electrolytes, the amounts of different substances deposited at the electrodes are in the ratio of their chemical equivalents.

If the same quantity of electricity is passed through three voltameters containing solutions of dil. H_2SO_4 , CuSO_4 , $5\text{H}_2\text{O}$ and AgNO_3 as shown in Fig. 10.20 then the masses of hydrogen, copper and silver deposited on respective cathodes will be in the ratio of their chemical equivalents.

Mass of copper deposited

Eq. mass of Cu

Mass of silver deposited

Eq. mass of Ag

Exercise 10.7: 0.2972 g of copper is deposited by a current of 0.5 ampere in 30 minutes. What is the electrochemical equivalent of Cu ?

Solution : Quantity of electricity passed $0.5 \times 30 \times 60 = 900$ coulomb.
Copper deposited by 900 coulomb = 0.2972 g. Copper deposited by 1 coulomb = $0.2972/900 = 0.00033$ g.

Hence, electrochemical equivalent of Cu = 0.00033 g

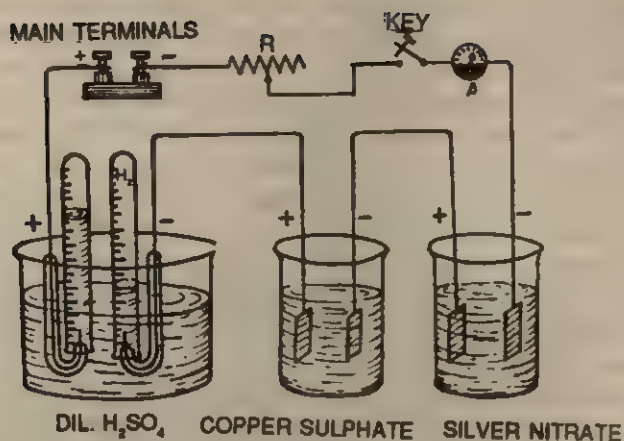


Fig. 10.20 : Electrolytic process

Exercise 10.8 : An electric current is passed through two cells in series containing solutions of copper sulphate and silver nitrate. What mass of Cu will be deposited while 4.26 g of Ag is being deposited ?

Solution :
$$\frac{\text{Mass of Ag deposited}}{\text{Mass of Cu deposited (X)}} = \frac{\text{Eq. mass of Ag}}{\text{Eq. mass of Cu}} \quad \frac{4.26}{X} = \frac{108}{31.7}$$

Therefore $X = 4.26 \times 31.7/108 = 1.25 \text{ g}$

10.7.3 Applications of Electrolysis

Electrolysis is used in the production of certain metals, *e.g.*, Na, K, Mg, Al, *etc.* (Unit 2, 14) and non-metals, *e.g.* chlorine *etc.* (Unit 13) purification of metals, *e.g.*, Cu, *etc.* (Unit 2, 15) and in electroplating.

Electroplating : In electroplating a uniform layer of a metal is formed on the surface of an object. As shown in Fig. 10.21 the object to be

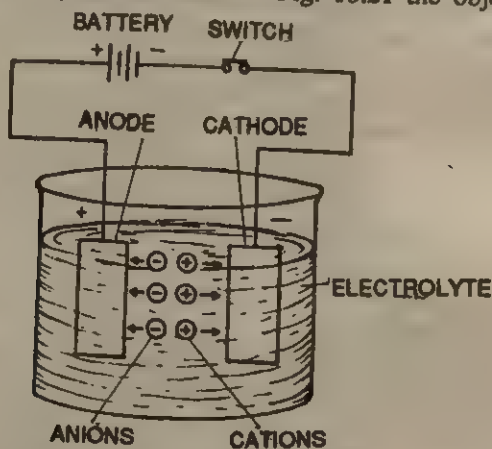


Fig. 10.21 : Electroplating of silver

electroplated is made cathode in the electrolytic cell and the plating metal is made anode. The electrolyte is a soluble plating metal salt. In the electroplating of silver on utensils, soluble silver salt is taken as the electrolyte. The electrode reactions are :

At the cathode : $\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$ deposited on utensil

At the anode : $\text{Ag} \longrightarrow \text{Ag}^+ + \text{e}^-$

Metals like gold, chromium, nickel, platinum, *etc.* can be electroplated on the surfaces of iron (steel) and copper. The electroplated objects resist corrosion. They can be used for decorative purposes also.

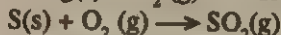
10.8 OXIDATION NUMBER

Let us consider the reaction.



The reaction is a case of oxidation as it involves the addition of oxygen. Here the substance being reduced is not readily seen. On the basis of electron transfer criterion and also if we remember that MgO is a network lattice of Mg^{2+} cations and O^{2-} anions, we find that the reaction may be regarded as oxidation of Mg to Mg^{2+} and reduction of oxygen to O^{2-} .

Now consider another reaction, which is formally a similar reaction to $2\text{Mg(s)} + \text{O}_2(\text{g}) \longrightarrow 2\text{MgO(s)}$, *i.e.*, burning of sulphur in oxygen.



This burning of sulphur cannot readily be regarded as an oxidation - reduction in the sense of complete electron transfer from one species to another. Nevertheless, it is desirable that this reaction should be viewed as a redox reaction, and this is possible through introducing an alternative definition in terms of directed numbers assigned to the atoms, called **oxidation numbers**. The use of such numbers provides a means of deciding whether oxidation - reduction is involved in a reaction or not. The change in oxidation number of a species indicates that oxidation or reduction has occurred. Oxidation numbers are a book-keeping concept introduced by chemists. The oxidation number, sometimes referred to as the oxidation state, is used to designate the positive and negative character of the atoms. Therefore, the oxidation number is a charge assigned to an atom of a compound or an ion according to some arbitrary rules. This number is only a convenience in case of covalent compounds. When valence electrons are removed or shifted away from an atom during a chemical reaction, the atom is assigned a positive oxidation number and is said to be in a positive oxidation state when electrons are gained or shifted toward an atom during a chemical reaction the atom is given a negative oxidation number and is said to be in a negative oxidation state. The numerical value of the oxidation number depends upon the number of electrons involved per atom in the transfer or shift to or away from the atom.

Rules for Assigning Oxidation Number

Oxidation number may be determined as follows :

- (1) The oxidation numbers of monoatomic ions are simply the charges of the ions. Thus, the oxidation numbers of the ions K^+ , Cl^- , Cu^{2+} , Fe^{3+} are +1, -1, +2, and +3 respectively.
- (2) The oxidation numbers of atoms which are not in the form of ions, *e.g.*, for S and O₂ in SO₂, are found from the following formal rules :
 - (i) Atoms of elementary substances/compounds are given an oxidation number of zero, *e.g.*, the oxidation number of Br in elementary Br₂ is zero. Others like H₂, P₄, S₈, O₂, N₂, F, Ag, K, *etc.* have oxidation number zero.
 - (ii) Hydrogen is assigned an oxidation number +1 in its compounds except when bonded to active metals as in NaH, where it assumes an oxidation number -1
 - (iii) Oxygen atom is generally given an oxidation number -2 in its compounds, except when it forms peroxide and fluoride. In case of Na₂O₂ (sodium peroxide) and H₂O₂ (hydrogen peroxide), the oxidation number of oxygen is -1. In case of OF₂, oxygen has an oxidation number +2. The oxidation numbers of all other species are deduced from these following rules.
3. For any neutral compound, the algebraic sum of the individual oxidation numbers assigned to atoms is zero.
4. For an ion (or polyatomic ion), the algebraic sum of the oxidation number of the atoms is the charge on the ion.
5. The more electronegative atom in the species has the negative oxidation number, the less electronegative atom has the positive number, *e.g.*, alkali metals in their compounds assume an oxidation number +1; alkaline earth metals +2 in their compounds; fluorine is assigned an oxidation number of -1 in all its compounds. For all other halogens the oxidation number is always -1 except when they are bonded to a more electronegative halogen or oxygen, *e.g.*, in IF₇ the oxidation number of iodine is +7.

Many elements exhibit more than one oxidation numbers in their various compounds. For example, iron assumes +2 in FeCl₂ and +3 in FeCl₃. Lead exhibits oxidation numbers of +2 and +4 in PbCl₂ and PbCl₄ respectively. The oxidation number of chlorine in each of the above compounds is -1. Chlorine, however, shows an oxidation number of +1 in HOCl, +3 in HClO₂, +5 in HClO₃ and +7 in HClO₄.

By applying these rules we can calculate the oxidation number of any atom in a molecule or ion. For example, in Na₂SO₄, the oxidation number of sulphur can be calculated from the known oxidation numbers of sodium and oxygen. The two sodium atoms each with an oxidation number of +1, total +2, the four oxygen atoms, each with an oxidation

number of -2, total -8. For the algebraic sum of the oxidation numbers to be zero, sulphur must have an oxidation number +6. For Na_2SO_3 , a similar calculation shows the oxidation number of sulphur to be +4; in H_2S the oxidation number of sulphur is -2. Several common oxidation numbers are summarized in Table 10.2

TABLE 10.2 : Example of common oxidation numbers

Element	Oxidation number
N_2	0
H	+1 (except -1 in hydrides; e.g., NaH)
Li	+1
Na	+1
Pb	+1
Mg	+2
Ca	+2
Al	+3
F	-1
Cl	+1
Br	+1, -1
I	+1, -1
<div style="display: flex; align-items: center;"> <div style="font-size: 3em; margin-right: 10px;">}</div> <div> (+1, and -1 in compounds with only two atoms, e.g., for Cl +1 in ClF and -1 in ICl. Variable oxidation numbers in compounds containing more than two atoms or more than two types of atoms, e.g., in ClF_3, Cl assumes +3 oxidation number; Cl assumes +7 in NaClO_4) </div> </div>	
O	-2 (except -1 in peroxides; e.g., H_2O_2 and Na_2O_2)
Hg	+1 and +2
Fe	+2 and +3
Cu	+1 and +2
Pb	+2 and +4

It is important to emphasize that, although the concept of oxidation numbers is of great convenience in writing formulae and in balancing oxidation and reduction equations, the concept of oxidation number is quite arbitrary.

Exercise 10.9 : Calculate the oxidation numbers of all the atoms in the following compounds and ions: CO_2 , Al_2O_3 , H_2SO_4 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, P_2O_5 , CH_2Cl_2 , NH_4^+ , $\text{Ca}(\text{OH})_2$ and K_2CO_3 .

Solution :

Species	Oxidation number	Oxidation number of atoms
CO_2	Each oxygen = -2 Total oxygen = -4	Total charge (=0) - total oxygen = -4 Carbon = +4
Al_2O_3	Each oxygen = -2 Total oxygen = -6	Total charge (=0) - (total oxygen = -6) Total Al = +6 Each Al = +3

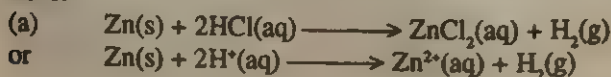
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Table (Continued)

Species	Oxidation number	Oxidation number of atoms
H_2SO_4	Total oxygen = -8 Total charge (=0) - [total (oxygen + hydrogen) = -6] Total Hydrogen = +2 Total (oxygen + hydrogen) = -6 Sulphur = +6	H = +1 O = -2 S = +6
KMnO_4	Total oxygen = -8 Potassium = +1 Total (oxygen + potassium) = -7 Total charge (=0) - [total (oxygen + potassium) = -7] Manganese = +7	K = +1 O = -2 Mn = +7
$\text{K}_2\text{Cr}_2\text{O}_7$	Total oxygen = -14 Total potassium = +2 Total (oxygen + potassium) = -12 Total charge (=0) - [total (oxygen + potassium) = -12] Total chromium = +12 Each chromium = +6	O = -2 K = +1 Cr = +6
P_2O_5	Total oxygen = -10 Total charge (=0) - [total (oxygen) = -10] Total phosphorus = +10 Each phosphorus = +5	O = -2 P = +5
CH_2Cl_2	Total chlorine = -2 Total hydrogen = +2 Total (chlorine + hydrogen) = 0 Total charge (=0) - [total (chlorine + hydrogen) = 0] Carbon = 0	H = +1 Cl = -1
NH_4^+	Each hydrogen = +1 Total hydrogen = +4 Total charge (= +1) - total hydrogen = +4 Nitrogen = -3	H = +1 N = -3
Ca(OH)_2	Total hydrogen = +2 Total oxygen = -4 Total (hydrogen + oxygen) = -2 Total charge (=0) - [total (hydrogen + oxygen) = -2] Calcium = +2	H = +1 O = -2 Ca = +2
K_2CO_3	Total oxygen = -6 Total potassium = +2 Total (oxygen + potassium) = -4 Total charge (=0) - [total (oxygen + potassium) = -4] Carbon = +4	O = -2 K = +1 C = +4

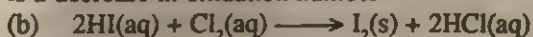
10.8.1 Redox Reactions in terms of Oxidation Number

A reaction is considered as a redox reaction if there is a change in the oxidation number. Let us consider, for example, the following reactions.



- Reactant :** Oxidation number of Zn = 0
 Total oxidation number of hydrogen = +2
- Product :** Oxidation number of Zn²⁺ = +2
 Oxidation number of dihydrogen = 0

The oxidation number of zinc has increased from 0 to +2. It has been oxidized. The oxidation number of hydrogen has been decreased +1 to 0 (for total hydrogen +2 to 0). It has been reduced. Thus, we conclude that oxidation is an increase in oxidation number and reduction is a decrease in oxidation number

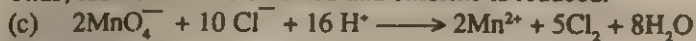


Change in oxidation numbers, I = -1 to 0,

Cl = 0 to -1

H = +1 to +1 (no change)

Thus, iodine in HI is oxidized and chlorine is reduced.

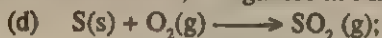


Change in oxidation number, Mn = +7 to 2

O = -2 to -2 (no change)

Cl = -1 to 0

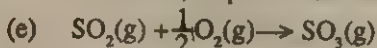
Therefore, manganese in MnO_4^- is reduced and Cl^- is oxidized.



Change in oxidation numbers, S = 0 to +4,

element O₂ = 0 to -2.

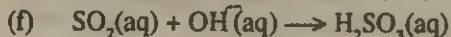
Therefore, sulphur is oxidized and elemental oxygen is reduced.



Change in oxidation numbers, S = +4 to +6,

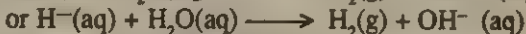
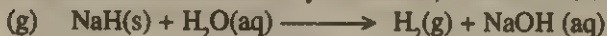
element O₂ = 0 to -2.

Therefore, the increase in oxidation number of sulphur shows this to be an oxidation reaction. Elemental oxygen has been reduced as its oxidation state decreases from 0 to -2.



Change in oxidation numbers, S = +4, to +4; O = -2 to -2

In this reaction, the oxidation state of each element remains unaltered and so this reaction by definition, is not a redox reaction.



Change in oxidation numbers :

H in the hydride ion = -1 to +1 in OH⁻ ion.

H in the water = +1 to 0 in H₂

In the reaction, hydrogen is experiencing both oxidation and reduction. The reaction is, therefore, one of oxidation and reduction. This reaction also represents, by definition, an acid-base reaction. Hence, the reaction may be regarded both as an acid-base reaction and as a redox reaction.

10.8.2 Oxidation Number and Nomenclature

During the development of chemistry, substances were often given names based on some characteristic property or on their structure without any relationship to their chemical nature, *e.g.*, blue vitriol ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), calomel (Hg_2Cl_2), quick silver (Hg), Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). Such trivial names are being replaced by more systematic names.

When an element forms more than one oxidation states, it is required to distinguish between the states. Older nomenclature uses the ending -ous to denote a lower oxidation state and the ending-ic to denote a higher oxidation state, *e.g.*, ferrous chloride (FeCl_2) and ferric chloride (FeCl_3). Neither of the two endings indicate a specific oxidation state. Therefore, it is preferable to use Roman numerals immediately following the modern name of the element to show its oxidation state (Table 10.3) as proposed by Albert Stock (1910-1936)

TABLE 10.3 Common and Stock names for some salts

Molecular formula	Common name	Stock name
FeCl_2	Ferrous chloride	Iron (II) chloride
FeCl_3	Ferric chloride	Iron (III) chloride
Cu_2O	Cuprous oxide	Copper (I) oxide
PbCl_2	Plumbous chloride	Lead (II) chloride
PbCl_4	Plumbic chloride	Lead (IV) chloride
$\text{K}_2\text{Cr}_2\text{O}_7$	Potassium dichromate	Potassium dichromate (VI)
V_2O_5	Vanadium pentoxide	Vanadium (V) oxide
Mn_2O_7	Manganese heptoxide	Manganese (VII) oxide

With the knowledge of oxidation state from the name of compounds it is easy to reconstruct the formula of the compound. For example, manganese (III) oxide is formed from Mn^{3+} cation and the O^{2-} anion. To make it neutral there must be two Mn^{3+} and three O^{2-} ions, hence, the formula is Mn_2O_3 .

Stock notation is not generally used for compounds formed from 2 nonmetals. Compounds such as PCl_3 and PCl_5 are differentiated by names phosphorus trichloride and phosphorus pentachloride respectively. It means if two elements form more than one binary compounds, Greek prefixes mono -(1) di- (2), tri-(3), tetra-(4), penta-(5), hexa-(6), *etc.* are used to designate the ratio of atoms in the compounds. Accordingly the oxides of nitrogen :

N_2O	Dinitrogen oxide (Nitrous oxide)
NO	Nitrogen oxide (Nitric oxide)
N_2O_3	Dinitrogen trioxide
NO_2	Nitrogen dioxide
N_2O_5	Dinitrogen pentoxide

10.8.3 Balancing of Oxidation Reduction Equations

Many compounds or ions in aqueous solutions generally act as oxidizing agents ($\text{Cr}_2\text{O}_7^{2-}$, MnO_4^- , Fe^{3+} , Cl_2) whereas other generally act as reducing agents (Zn , SO_3^{2-} , Sn^{2+} , Fe^{2+}). A large number of possible redox reactions arise from different types of combinations of pairs of oxidizing and reducing agents. It is advisable to frame a working procedure which helps in balancing chemical reactions.

Many equations for oxidation and reduction reactions such as those between zinc and chlorine or between iron and oxygen can be balanced readily, by inspection. The balancing of redox reactions equations come across in electrochemical cells could also be done by inspection. Such reactions occur in two steps and we denote them by two half-cell reactions. Oxidation reaction occurs in one half-cell and reduction reaction occurs in the other half. At times, the equations which represent these half-cell reactions are called partial equations. Let us take the help of these partial equations in balancing non-electrochemical redox reactions. For balancing such redox reactions : (i) we first write the balanced partial (or half) equation, (ii) partial equations are combined to obtain an overall balanced reaction equation taking care to balance electrons as well.

Rules for Balancing a Redox Reaction Equation :

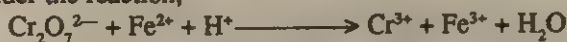
1. Knowledge of the correct molecular formulae of the oxidizing (oxidant) and reducing (reductant) agents and also that of reduced and oxidized products is desired.
2. The law of conservation of mass should be adhered to.
3. Balancing of electrons should be done carefully.

Redox reactions occur in acidic, basic and neutral solutions. In balancing such reactions one has to take care that H^+ or any acid, OH^- or any base or none appear on either side of the equation.

The equations for complex reactions can also be balanced easily by considering the reaction in two partial equations or more. At times, it is not easy to write down a partial reaction when polyatomic ions are involved, e.g., it is not obvious what the partial reactions are for the dichromate - chromium (III) and permanganate - manganese redox pairs in acid solution. To arrive at partial reaction equations for such systems, the use of formal oxidation numbers is necessary. A equation can be achieved by considering the following points :

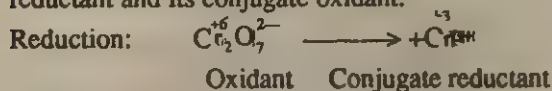
1. Change in oxidation numbers (or states) that occurs.
2. For oxidation to take place, reduction must occur.
3. Number of electrons lost by the reductant must equal the number gained by oxidant

For illustrating the method of balancing a redox reaction, let us consider the reaction,

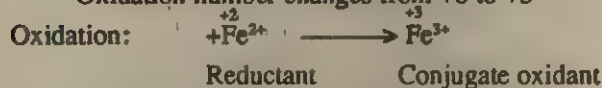


To arrive at a balanced equation let us proceed stepwise.

STEP - I : Find the elements whose oxidation numbers are changed. To do this first write down the oxidant and its conjugate reductant, and then reductant and its conjugate oxidant.



Oxidation number changes from +6 to +3



Oxidation number changes from +2 to +3

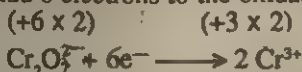
STEP - II: Balance each half-equations separately. Let us first consider the reduction half-equation.

(i) Balance with respect to the atom which is undergoing a change in oxidation number. There are two Cr atoms on the left, one on the right. Hence, $\text{Cr}_2\text{O}_7^{2-} \longrightarrow 2 \text{Cr}^{3+}$

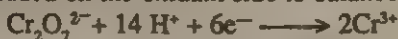
(ii) Assign and calculate the total oxidation numbers of the atom undergoing a change in oxidation number



(iii) Balance the oxidation numbers by adding electrons to which ever side is necessary to make up for the difference. The total oxidation number for chromium atoms is +12 on the left and on the right +6. Therefore add 6 electrons to the oxidant side of the equation.,



(iv) Balance the half-equation in the terms of the charges. Since reaction is taking place in acid solution, H^+ ion is necessary to be added to account for the extra positive charge on either side. The total charge on the left is -8, on the right side +6. Therefore 14H^+ should be added on the oxidant side to balance the charge.



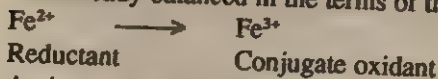
(v) Balance oxygen by adding water. Since there are 14 hydrogen atoms and 7 oxygen atoms on the left side, $7\text{H}_2\text{O}$ is needed on the right,



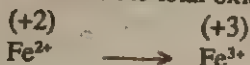
Notice, that the equation is now balanced.

Now let us take the oxidation half-equation and apply the same steps.

- (i) It is already balanced in the terms of the atoms.



- (ii) Assign and calculate the total oxidation numbers.

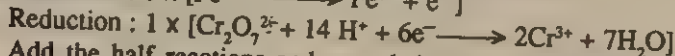
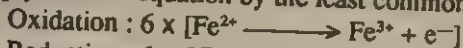


- (iii) Balance the oxidation number by adding one electron to the conjugate oxidant side.

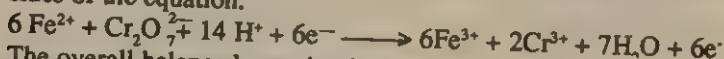


- (iv) Balance the equation for the charges. Both sides have already achieved balance for the charges, i.e., +2 on both the sides.
(v) Addition of water is not required as this half-reaction does not involve oxygen and hydrogen.

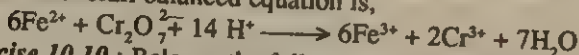
STEP-III: Before combining, ensure that the number of electrons lost by the reducing agent must equal the number gained by the oxidizing agent, i.e., change experienced, in terms of oxidation number, by oxidation reaction must equal the change in a reduction reaction. If necessary, multiply the half equation by the least common multiple.



Add the half reactions and cancel the terms that appear on both sides of the equation.



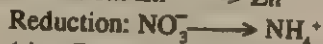
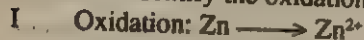
The overall balanced equation is,



Exercise 10.10 : Balance the following equation in a basic solution



Solution : Identify the oxidation and reduction reactions.



II (a) **Balance the Oxidation Half-Reaction**

- (i) Balance the equation with respect to atoms (other than H and O). It is already balanced.

- (ii) Calculate the oxidation number



- (iii) Balance the oxidation numbers by adding electrons.



- (iv) Balance the charges : already balanced.

- (v) Not required as it does involve oxygen.

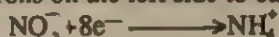
(b) **Balance the Reduction Half-Reaction**

- (i) Balance the equation with respect to atoms other than H and O : already done.

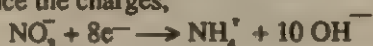
- (ii) Calculate the oxidation number of the atoms undergoing change in oxidation numbers.



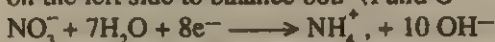
- (iii) Balance the oxidation number by adding electrons. For N oxidation number changes from +5 to -3. Therefore, add 8 electrons on the left side to balance the oxidation number.



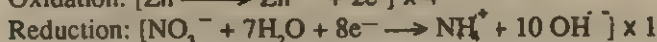
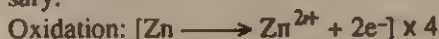
- (iv) Balance the charges. In basic solution OH^- are required to account for extra negative charges. Total charge on left is -9, on the right +1. Therefore add ten OH^- on the right side to balance the charges,



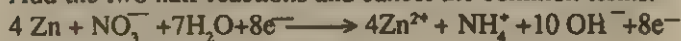
- (v) Add water molecules to balance oxygen. There are 3 oxygen on the left side and 10 oxygen on the right side. Add $7\text{H}_2\text{O}$ on the left side to balance both H and O



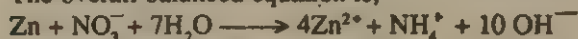
- III (i) Now balance the electrons produced in oxidation and consumed in reduction. Multiply the equation by some least common multiple number to balance the electrons if necessary.



- (ii) Add the two half-reactions and cancel the common terms.

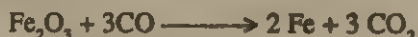


The overall balanced equation is,



10.8.4 Applications of Redox Reactions

- I In metallurgical operations : Metal oxides are reduced to metals by using appropriate reducing agents. Purified iron ore (Fe_2O_3) is reduced by carbon monoxide (from coke by air oxidation) in a blast furnace.



Aluminium, sodium, calcium, magnesium and potassium are obtained by employing electrolytic (or cathodic) reduction method. Both zinc and lead are also produced by reducing their oxides with carbon.

- Reaction of hydrogen and oxygen is used in fuel cells (electrochemical cells with hydrogen and oxygen electrodes). Fuel cells are used to supply electrical energy in space capsule.
- Trees grow by chemical change, carbon dioxide from the air combines with water to make new cells. This is the basis of a reaction called **photosynthesis** and needs the energy from its surrounding particularly sun to make it work.

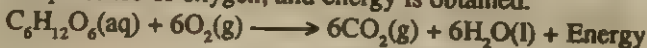


Here CO_2 is reduced to carbohydrate and water is oxidized to oxygen with sun supplying the energy.

4. All energy supplies are possible through redox reactions. Power stations and domestic fires get energy through coke. Engines of all sorts, e.g., cars, ships, aeroplanes, etc., use oil to get energy. For cooking etc., gas gives energy. All these fuels give energy through their oxidation.

Fuels (wood, gas, oil, etc.) + $\text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Energy} + \text{other products}$.

In living cells, glucose $\text{C}_6\text{H}_{12}\text{O}_6$ is oxidized to CO_2 and water in the presence of oxygen, and energy is obtained.



SELF ASSESSMENT QUESTIONS

MULTIPLE CHOICE QUESTIONS

10.1 Put a (✓) mark against the suitable answer :

- (i) A solution containing one mole per litre each of $\text{Cu}(\text{NO}_3)_2$, AgNO_3 , $\text{Hg}_2(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ is electrolysed using inert electrodes. E° in volt (reduced potential) are : $\text{Ag}^+/\text{Ag} = 0.80$, $\text{Cu}^{2+}/\text{Cu} = 0.34$, $\text{Hg}_2^{2+}/2\text{Hg} = 0.79$, $\text{Mg}^{2+}/\text{Mg} = -2.37$. With increasing voltage, the sequence of deposition of metals on the cathode will be :
 (a) Ag, Hg, Cu, Mg, (b) Mg, Cu, Hg, Ag,
 (c) Ag, Hg, Cu, (d) Cu, Hg, Ag, (IIT 1984).
- (ii) The electric charge for electrode deposition of one gram equivalent of a substance is : (IIT 1984)
 (a) one ampere for one second (b) 96,500 coulombs per second, (c) one ampere for one hour (d) charge on one mole of electrons
- (iii) The reaction $1/2 \text{H}_2(\text{g}) + \text{AgCl}(\text{s}) \longrightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Ag}(\text{s})$ occurs in the galvanic cell. (IIT 1985)
 (a) $\text{Ag} | \text{AgCl}(\text{s}) | \text{KCl solution} | \text{AgNO}_3(\text{aq}) | \text{Ag}$
 (b) $\text{Pt} | \text{H}_2(\text{g}) | \text{HCl solution} | \text{AgNO}_3(\text{aq}) | \text{Ag}$
 (c) $\text{Pt} | \text{H}_2(\text{g}) | \text{HCl solution} | \text{AgCl}(\text{s}) | \text{Ag}$
 (d) $\text{Pt} | \text{H}_2(\text{g}) | \text{KCl solution} | \text{AgCl}(\text{s}) | \text{Ag}$
- (iv) When a lead storage battery is discharged, (IIT 1987)
 (a) SO_2 is evolved (b) lead is formed (c) lead sulphate is consumed (d) sulphuric acid is consumed.
- (v) The standard reduction potential, E° for the half-reactions are as, (IIT 1988)
 $\text{Zn}^{2+}/\text{Zn} \quad E^\circ = +0.76 \text{ V}$
 $\text{Fe}^{2+}/\text{Fe} \quad E^\circ = -0.41 \text{ V}$
 The emf for the cell reaction $\text{Fe}^{2+} + \text{Zn} \longrightarrow \text{Zn}^{2+} + \text{Fe}$... is
 (a) -0.35 V (b) $+0.35 \text{ V}$ (c) $+1.17 \text{ V}$ (d) -1.17 V
- (vi) Which of the following reactions occur at the cathodes ?
 (a) hydrolysis (b) oxidation (c) reduction (d) none
- (vii) The reaction $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$ occurs
 (a) at the anode (b) at the cathode (c) in solution (d) not possible

- (viii) One Faraday is equal to
 (a) 96.5 coulombs mol^{-1} (b) 96.5×10^{23} coulombs mol^{-1} (c) 6.23×10^{23} coulombs mol^{-1} (d) 96500 coulombs mol^{-1}
- (ix) Which of the following ions move towards the anode during electrolysis of brine solution?
 (a) Na^+ ions (b) Cl^- ions (c) OH^- ions (d) H^+ ions
- (x) Which of the following processes is an oxidation process?
 (a) the increase in positive charge of an ion
 (b) the addition of hydrogen to a compound
 (c) the addition of chlorine to a compound
 (d) the loss of hydrogen ions by an acid
- (xi) The following are balanced half-reaction equations, which of them represent reduction process?
 (a) $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{e}^-$
 (b) $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
 (c) $\text{H}_2\text{S} \longrightarrow \text{S} + 2\text{H}^+ + 2\text{e}^-$
 (d) $4\text{OH}^- \longrightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$
- (xii) To balance the equation
 $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + \text{Z}\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$, Z should be given a value of
 (a) 4 (b) 5 (c) 6 (d) 7
- (xiii) For the following reaction in acidic solution
 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
 which of the following gives the true oxidation numbers of the manganese on each side of the equation?
 (a) +7 to +6 (b) +7 to +2 (c) +4 to +2 (d) -2 to +2
- (xiv) Which of the following metals is obtained industrially by electrolytic reduction?
 (a) Iron (b) Aluminium (c) Copper (d) Zinc.
- (xv) Which of the following reactions could not be termed redox reactions.
 (a) $2\text{NaCl(s)} + \text{H}_2\text{SO}_4\text{(aq)} \longrightarrow \text{Na}_2\text{SO}_4\text{(aq)} + \text{HCl(aq)}$
 (b) $\text{S(s)} + \text{O}_2\text{(g)} \longrightarrow \text{SO}_2\text{(g)}$
 (c) $2\text{Na(s)} + \text{Cl}_2\text{(g)} \longrightarrow 2\text{NaCl(s)}$
 (d) $\text{H}_2\text{S(g)} + \text{O}_2\text{(g)} \longrightarrow \text{H}_2\text{O(g)} + \text{S(s)}$

10.2 Fill in the blanks with appropriate words

- The more the standard reduction potential, the is its ability to displace hydrogen from acids.
- The process whereby the electrical energy is used to bring about a chemical reaction is called
- As the reductant loses electrons it is oxidized, and as the oxidant
- The positive electrode in an electrolytic cell is called
- In reactions the number of electrons and must be equal.
- The chemical reaction for the Daniel's cell
- An oxidizing substance causes another substance to
- takes place in the presence of sunlight.
- The potential difference between the standard hydrogen electrode and another electrode is called
- The negative electrode where occurs is called

10.3 Choose True and False statements of the followings :

- Pb^{2+} is a better oxidizing agent than Cu^{2+}
- In the reaction $\text{Cu} + \text{Br}_2 \longrightarrow \text{CuBr}_2$, copper is oxidized and Br is reduced.
- A mutual exchange of electrons gives rise to a redox reaction.
- A couple in isolation will maintain its reversible equilibrium.
- A couple $\text{Fe}^{3+}/\text{Fe}^{2+}$ cannot undergo both oxidation and reduction process.
- Electrode potential does not depend upon concentration.
- A flow of electron constitutes an electric current.

- (viii) Oxidation refers to gain of electrons.
- (ix) An oxidation number does not predict the oxidation state of an element.
- (x) The shifting of electrons towards an atom in a covalent bond is called oxidation.

10.4 Match the statements listed under column B against the terms given under column A.

Column A	Column B
1 Leclanche cell	a. Cells are connected in series
2 Lead storage battery	b. A dry cell
3 Daniel cell	c. A galvanic cell
4 Watt	d. A unit of electrode potential
5 Volt	e. A unit of electrical energy
6 Porous diaphragm	f. An effective way of separating ions from mechanical mixing.
7 Salt bridge	g. Avoids diffusion of ions
8 Anode	h. Oxidation reaction takes place
9 Cathode	i. Reduction reaction takes place

SHORT ANSWER QUESTIONS

- 10.5 (i) Which of the following reactions are redox reactions ?
Identify the oxidizing and the reducing agents in the redox reaction.
- (a) $I_2(s) + H_2S(g) \longrightarrow 2HI(g) + S(s)$
 - (b) $Pb^{2+}(aq) + 2I^-(aq) \longrightarrow PbI_2(s)$
 - (c) $SO_2(aq) + NO_2(aq) \longrightarrow SO_3(aq) + NO(aq)$
 - (d) $NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$
 - (e) $2Cl_2(g) + CH_4(g) \longrightarrow 4HCl(g) + C(s)$
- (ii) Give the oxidation state of :
(a) Fe in $FeCl_3$, (b) N in HNO_3 , (c) Cl in $NaClO_4$, (d) P in PO_4^{3-}
- (iii) Give the cell notation for the reaction
 $Sn(s) + 2H^+(aq) \longrightarrow Sn^{2+}(aq) + H_2(g)$
- (iv) A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of $10^{-6} M$ hydrogen ions. The emf of the cell is 0.118V at 298K. Calculate the concentration of H^+ ions at the positive electrode. (IIT 1988)
- (v) Predict from the table of standard electrode potential whether the following reactions occur :
- (a) Will $Mg(s)$ displace Sn^{2+} from aqueous solution ?
 - (b) Will copper(s) reduce Ag^+ ion aqueous solution ?
 - (c) $Pb^{2+}(aq) + 2Ag(s) \longrightarrow 2Ag^+(aq) + Pb(s)$
 - (d) $2Ag^+(aq) + Pb(s) \longrightarrow 2Ag(s) + Pb^{2+}(aq)$
 - (e) Will copper(s) dissolve in 1M HCl ?
 - (f) Will $Zn(s)$ displace $Al(aq)$ from solution ?
- (vi) The following cell has $E^\circ = 0.66 V$. The Fe^{2+}/Fe electrode is the anode.
 $Fe \parallel Fe^{2+} \parallel Cl^- \parallel AgCl \parallel Ag$. Calculate its E° value.
- (vii) What oxidizing agents could be employed in 1M solution to oxidize Br^- to Br_2 ?
- (viii) Write the half reaction equations for the following redox reactions.
- (a) $Zn(s) + PbCl_2 \longrightarrow Pb(s) + ZnCl_2(aq)$
 - (b) $2Fe^{3+}(aq) + 2I^- \longrightarrow I_2(aq) + 2Fe^{2+}(aq)$
 - (c) $2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$
 - (d) $Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$
 - (e) $Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+} + 4H_2(g)$
- (ix) On the basis of the above question answer the following questions.
- (a) Which reactant is oxidized? Give the oxidized product ?
 - (b) Which reactant is the oxidant ?
 - (c) Which reactant is reduced and to what ?
 - (d) Which reactant is the reductant ?

- (x) The charge of an electron is 1.60219×10^{-19} coulombs. Calculate the value of the Faraday constant F .
- 10.6 (a) Calculate the emf of the cells formed by the various combinations of the following standard half-cells. (concentration is 1 mol L^{-1})
- (i) $Zn(s) | Zn^{2+}(aq)$ (iv) $Ni(s) | Ni^{2+}(aq)$
 (ii) $Cr(s) | Cr^{3+}(aq)$ (v) $Cu(s) | Cu^{2+}(aq)$
 (iii) $Cu(s) | Cu^{2+}(aq)$ (vi) $Ag(s) | Ag^{+}(aq)$
- (b) Give the anodic and cathode reactions for the followings. Indicate the positive terminal in each case.
- (i) $Zn(s) | Zn^{2+} || Br^{-} | Br_2(g) | Pt(s)$
 (ii) $Cr(s) | Cr^{3+} || I^{-}, I_2 | Pt(s)$
 (iii) $Pt(s) | H_2(g) || H^{+}(aq) | Cu^{2+} | Cu(s)$.
- (c) Calculate the emf of the cell $Pb(s) | Pb(NO_3)_2(M_1) | HCl(M_2) | H_2(g) | Pt(s)$
 When $M_1 = 0.1M$, $M_2 = 0.2M$ and $\rho_{H_2} = 1$ atm
- (d) With the help of Table 10.1, choose an appropriate oxidizing agent capable of converting :
- (i) Cl^{-} to Cl_2 (ii) I^{-} to I_2
 (iii) Pb to Pb^{2+} (iv) Fe^{2+} to Fe^{3+}
- (e) With the help of Table 10.1, choose an appropriate reducing agent capable of converting
- (i) Fe^{3+} to Fe (ii) Ag^{+} to Ag (iii) Al^{3+} to Al
- (f) How long a current of 3 ampere has to be passed through a solution of silver nitrate to coat a metal surface of 80 cm^2 with a 0.005 mm thick layer?
 Density of silver is 10.5 g/cm^3 (IIT 1985)

TERMINAL QUESTIONS

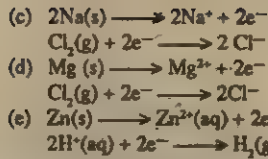
- 10.1 (a) Arrange the metal listed below in a decreasing order of the reactivity. Point out the strongest and the weakest reducing agents. Cd, Ag, Sn, K, Zn, Cu, Pb
- (b) As per the values of E° for Na and Mg, sodium metal should displace Mg^{2+} from aqueous solution but in practice it does not occur. Comment?
- 10.2 (a) When a copper metal rod is immersed in a silver nitrate solution, copper ions start appearing in the solution and silver metal gets deposited on the rod. Can the copper rod be regarded an electrode? If so, is it an anode or a cathode?
- (b) The following hypothetical metals have been assigned E° as given against each. Which would displace H_2 gas from 1 M HCl solution?
- | Metal | $E^{\circ}(V)$ |
|-------|----------------|
| A | -2.4 |
| B | +2.1 |
| C | -0.3 |
| D | +0.1 |
| E | -3.7 |
- Which of the metals would reduce A^{2+} ions to A metal in a 1M A^{2+} solution?
- 10.3 Zinc displaces H_2 from 1 M HCl but copper does not. If a pair of copper and zinc (joined together) metals is immersed in 1M HCl solution, bubbles of H_2 gas appear at the copper metal. (a) Does it mean that copper displaces H_2 from HCl (aq)? (b) What is the reaction that occurs? (c) What is the role of the copper metal?
- 10.4 In each of the following examples, draw a diagram of galvanic cell that uses the given reaction. Mark the anode and the cathode. Show the direction of flow of electrons. Write the balanced equation for each cell reaction. Calculate E°_{cell}
- (a) $Ag^{+}(aq) + Fe^{2+}(aq) \longrightarrow Ag(s) + Fe^{3+}(aq)$
 (b) $Cu(s) + Cl_2(g) \longrightarrow Cu^{2+}(aq) + 2 Cl^{-}(aq)$
 (c) $Zn(s) + 2Ag^{+}(aq) \longrightarrow Zn^{2+} + 2Ag(s)$
 (d) $Cu^{2+}(aq) + H_2(g) \longrightarrow 2H^{+}(aq) + Cu(s)$

- 10.5 A traditional way of writing Daniel cell is :
 $\text{Zn(s)} ; \text{Zn}^{2+}(\text{aq}) (\text{1M}) || \text{Cu}(\text{aq}) (\text{1M}) ; \text{Cu(s)}$
 (a) Draw a diagram of the cell and label the anode and the cathode ?
 (b) Indicate the direction of electron flow ?
 (c) Give the redox reaction ?
 (d) Calculate the cell potential at 298K.
- 10.6 Define the following terms : (a) Electrochemistry, (b) Cathode, (c) Anode, (d) Electrolytic cell, (e) Battery, and (f) Electrode potential.
- 10.7 Discuss the principle of operation of a galvanic cell with respect to the followings :
 (a) nature of current, (b) reactions both at anode and cathode, (c) movement of ions, (d) discharge of ions, and (e) half-cell reaction.
- 10.8 (a) Distinguish clearly between ampere, watt, coulomb and volt. How are they related?
 (b) State the meaning of electrode potential. Mention the factors which affect the electrode potential
- 10.9 (a) State the primary requirement of a cell which can furnish a continuous flow of electrons.
 (b) Describe two commercial galvanic cells with the half-cell reactions occurring at each electrode.
- 10.10 Define standard electrode potential. Suggest a method for finding the standard electrode potential of a conductor.
- 10.11 (a) State reasons for keeping the ion concentration and the temperature fixed for measuring standard electrode potential.
 (b) Describe standard hydrogen electrode.
- 10.12 Give the Nernst equation and describe its applications with some examples.
- 10.13 Discuss the reduction potential table with reference to the followings : (a) Placements of the elements, ions and molecules, (b) Reducing agents and oxidizing agents, (c) coupling of the various half-cells to set up a galvanic cell, (d) Behaviour of some substances both as oxidizing and as reducing agents, (e) Defects of the table, and (f) Applications of the table.
- 10.14 (a) What is an electrochemical series? List some of its uses ? (b) Show by appropriate equations that the electrode reaction for the zinc electrode is a reversible one.
- 10.15 Define the following terms with illustrations :
 (a) Oxidation, (b) Reduction, (c) Half-cell reaction, (d) Oxidizing agent, (e) Reducing agent, and (f) Salt bridge.
- 10.16 Write short notes on the following :
 (a) Oxidation and reduction potentials, (b) Standard hydrogen electrode, (c) Electrochemical changes, and (d) Daniel cell.
- 10.17 Distinguish clearly between the following pairs :
 (i) Electron movement and ion movement, (ii) emf and potential difference (iii) Electrochemical cell and electrolytic cell, (iv) Cathode and anode.
- 10.18 (a) Define oxidation number. What is its significance for covalent compounds.
 (b) State the oxidation numbers of the underlined elements in each of the following ions :
 HSO_3^- , HSO_4^- , MnO_4^- , CrO_4^{2-} , BO_3^{3-} , $\text{C}_2\text{O}_4^{2-}$
- 10.19 Decide which of the followings may be regarded as redox reactions ?
 (i) $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + 2\text{HCl}$
 (ii) $2\text{Ag} + \text{Cl}_2 \longrightarrow 2\text{AgCl}$
 (iii) $2\text{FeCl}_3 + \text{SnCl}_2 \longrightarrow 2\text{FeCl}_2 + \text{SnCl}_4$
 (iv) $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$
 (v) $4\text{NH}_3 + \text{SO}_2 \longrightarrow 4\text{NO} + 6\text{H}_2\text{O}$
- 10.20 (a) Copper metal reacts with nitric acid to $\text{Cu}(\text{NO}_3)_2$, NO, and H_2O . Write the balanced reaction for the reaction making use of the rules for balancing the equation.
 (b) Write a short note on nomenclature of the compounds ?

- 10.21 What are the standard electrode potentials for cells in which the following reactions occur :
- (a) $\text{Mg(s)} + \text{Cd}^{2+}(\text{aq}) \longrightarrow \text{Mg}^{2+}(\text{aq}) + \text{Cd(s)}$ (Ans. $E^\circ = 1.98 \text{ V}$)
- (b) $\text{Fe(s)} + \text{Sn}^{2+}(\text{aq}) \longrightarrow \text{Fe}^{2+}(\text{aq}) + \text{Sn(s)}$ (Ans. $E^\circ = 0.30 \text{ V}$)
- (c) $2\text{Cr(s)} + 3\text{Cu}^{2+}(\text{aq}) \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{Cu(s)}$ (Ans. $E^\circ = 1.08 \text{ V}$)
- (d) $\text{H}_2(\text{g}) + 2\text{Ag}^+(\text{aq}) \longrightarrow 2\text{Ag(s)} + 2\text{H}^+(\text{aq})$ (Ans. $E^\circ = 0.80 \text{ V}$)
- 10.22 Calculate the standard electrode potential of Cl^- at 0.010M to Cl_2 at 5.0atm ($T = 25^\circ\text{C}$) (Ans. $E^\circ = 1.5 \text{ V}$)
- 10.23 What will be the reduction potential for hydrogen if it exerts one atmospheric pressure over a 0.001M solution of HCl ? (Ans. $E^\circ = -0.18 \text{ V}$)
- 10.24 Calculate the standard cell potential for the following electrode pairs :
- (a) Pb^{2+}/Pb and Sn^{2+}/Sn (Ans. 0.01 V)
- (b) Zn^{2+}/Zn and Cu^{2+}/Cu (Ans. 1.10 V)
- (c) $\text{H}_2(1 \text{ atm})/\text{H}^+$ and Cu^{2+}/Cu (Ans. 0.34 V)
- (d) Mg^{2+}/Mg and Cu^{2+}/Cu (Ans. 2.72 V)
- 10.25 Calculate emf of a Daniel cell consisting of a zinc electrode in the contact of 0.01 M solution of ZnSO_4 and a copper electrode dipped in a 1.5M solution of copper sulphate (1.10 V)
- 10.26 Will H_2 react with Pb^{2+} at standard conditions ?
 $E^\circ = -0.13 \text{ V}$ for $\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb}$ (Ans. No. Pb will react with H^+)
- 10.27 Calculate the emf of the following cell and write the equation for the cell reaction. Comment on the result
 $\text{Pb}; \text{Pb}^{2+}(1\text{M}) // \text{Ag}^+(1\text{M}); \text{Ag}$ (Ans. $E^\circ_{\text{cell}} = -0.93 \text{ V}$)

ANSWERS TO SELF ASSESSMENT QUESTIONS

- 10.1 (i) (c) (ii) (d) (iii) (c), (iv) (d) (v) (b) (vi) (c) (vii) (a) (viii) (d) (ix) (b) (x) (a) (xi) (b) (xii) (c) (xiii) (b) (xiv) (b) (xv) (a)
- 10.2 (i) negative, greater (ii) electrolysis (iii) gains electrons, it is reduced. (iv) Anode (v) Oxidation-reduction, lost, gained, (vi) $\text{CuSO}_4 + \text{Zn} \longrightarrow \text{ZnSO}_4 + \text{Cu}$ (vii) lose electrons (viii) Photosynthesis (ix) standard electrode potential (x) reduction, cathode.
- 10.3 (i) False (ii) True (iii) True (iv) True (v) False (vi) False (vii) True (viii) False (ix) False (x) False
- 10.4 1. b 2. a 3. c 4. e 5. d 6. g 7. f 8. h 9. i
- 10.5 (i) Oxidizing agent Reducing agent
 (a) I_2 H_2S
 (c) NO_2 SO_2
 (e) Cl_2 CH_4
- (ii) (a) $\text{Fe} = +3$ (b) $\text{N} = +5$ (c) $\text{Cl} = +7$ (d) $\text{P} = +5$ (iii) $\text{Sn} / \text{Sn}^{2+} // \text{H}^+ / \text{H}_2 / \text{Pt}$
- (iv) Let the concentration of the H^+ at the positive electrode be $A \text{ mol L}^{-1}$
 $E_2 = E^\circ + 0.0592 \log A$
 $E_1 = E^\circ + 0.0592 \log 10^{-6}$
 $E_2 = E_1 = 0.0592 (\log A - \log 10^{-6})$
 $0.118 = 0.592 (10 A - \log 10^{-6})$
 $A = 10^{-4} \text{ mol L}^{-1}$
- (v) (a) Yes (b) Yes (c) No (d) Yes (e) No (f) No
- (vi) Since $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$
 $0.66 = 0.22\text{V} = E^\circ_{\text{anode}}$
 $E^\circ_{\text{anode}} = 0.22\text{V} - 0.66\text{V} = -0.44 \text{ V}$
- (vii) Any of the reagents below Br_2 in Table 10.1 would cause the oxidation, e.g., MnO_2 , $\text{Cr}_2\text{O}_7^{2-}$, Cl_2 water, O_2
- (viii) (a) $\text{Zn(s)} \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$
 $\text{PbCl}_2(\text{aq}) + 2\text{e}^- \longrightarrow \text{Pb(s)} + 2\text{Cl}^-$
 (b) $2\text{Fe}^{3+}(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Fe}^{2+}(\text{aq})$
 $2\text{I}^-(\text{aq}) \longrightarrow \text{I}_2(\text{aq}) + 2\text{e}^-$



(ix) (a) Zn to Zn^{2+} (b) 2I^- (c) Cl_2 to 2Cl^- (d) 2H^+

(x) 1 Faraday = 1.0 mole = 6.023×10^{23}

1 electron = 1.602×10^{-19} coulombs

6.02×10^{23} electrons = $6.023 \times 10^{23} \times 1.60 \times 10^{-19}$

= $9.6488 \times 10^4 = 1$ Faraday

10.6 B(a) By combining (i) and (iv)

i.e. $E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}$ and $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= -(0.25) - (-0.76)$$

$$= -0.25 + 0.76 = 0.51 \text{ V}$$

By combining (ii) and (v)

$E^\circ_{\text{Co}^{2+}/\text{Co}} = -0.28 \text{ V}$; $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = -0.74 \text{ V}$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= 0.28 - (-0.74)$$

$$= -0.28 + 0.74 = 0.46 \text{ V}$$

By combining (iii) and (vi)

$E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V}$; $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

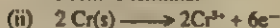
$$= 0.80 - 0.34$$

$$= 0.46 \text{ V}$$

(b) Reaction at anode



Positive terminal



Positive terminal



Positive terminal

Reaction at cathode



$\text{Br}^-/\text{Br}_2 \mid \text{Pt(s)}$

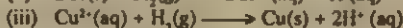


$\text{I}^-/\text{I}_2/\text{Pt(s)}$



Cu(s)

Cell reaction: (i) $\text{Zn(s)} + \text{Br}_2(\text{g}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Br}^-(\text{aq})$



(c) The cell reaction,



$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{H}_2} - E_{\text{Pb}}$$

By using the Nernst equation,

$$E_{\text{H}_2} + \frac{0.0592}{2} \log [\text{H}^+]^2 - \left[E_{\text{Pb}} + \frac{0.059}{2} \log [\text{Pb}^{2+}] \right]$$

Substituting the value for E_{H_2} and E_{Pb} from the Table 10.1

$$E_{\text{cell}} = 0 - (-0.13) + \frac{0.059}{2} \log [0.2]^2 / [0.1]$$

$$= 0.13 - 0.0112 = 0.1188 \text{ V}$$

(d) (i) Cl^- to Cl_2

(ii) I^- to I_2

(iii) Pb to Pb^{2+}

(iv) Fe^{2+} to Fe^{3+}

Oxidizing Agent

$\text{Au, F}_2, \text{Mn}_2, \text{MnO}_4^-$

$\text{Fe, Ag, Cl}_2, \text{Br}_2, \text{MnO}_2$

$\text{Cu, I}_2, \text{MnO}_4^-$

$\text{Ag, Cl}_2, \text{MnO}_4^-, \text{Br}_2$

	Reducing agent
(e) Fe^{2+} to Fe	Cu, Zn, Pb, etc.
Ag^+ to Ag	Fe, Cu, I, Sn, etc.
Al^{3+} to Al	Mg, Ca, etc.
(f) Volume of silver deposited	= Area \times thickness = $80 \times 0.05 = 0.4$ cc
Mass of silver deposited	= Volume \times density = $0.4 \times 10.5 = 4.2$ g = 108 amu

Amount of charge required to deposit 108 g of silver = 96500 C

Amount of charge required to deposit 4.2g of Ag = $96500 \times 4.2/108 = 3752$ C

Current = Charge/time

Time required to allow a current of 3A = $3752/3 = 1250$ s

UNIT 11

Rates of Chemical Reactions

.....a molecular system (passes) ... from one state of equilibrium to another by means of all possible intermediate paths, but the path, most economical of energy will be more often travelled.

Henry Eyring

UNIT PREVIEW

- 11.1 Introduction
- 11.2 Feasibility of a reaction
- 11.3 Rate of reaction
 - 11.3.1 Meaning of reaction rate
 - 11.3.2 Units of reaction rate
 - 11.3.3 Ways to measure reaction rate
 - 11.3.4 Average rate of reaction
 - 11.3.5 Determination of instantaneous rate
 - 11.3.6 Time dependence of reaction rate
- 11.4 Slow and fast reactions
- 11.5 Factors affecting rate of reaction
 - 11.5.1 The nature of the reactants
 - 11.5.2 Factors affecting the number of collisions between the reacting molecules
 - (i) Concentration of reactants
 - (ii) Surface area or state of aggregation
- 11.6 The quantitative effect of concentration-The order of a reaction
- 11.7 The temperature effect on reaction rate
 - 11.7.1 Theory of absolute reaction rate and activation energy (transition rate theory)
- 11.8 Catalysts
- 11.9 Effect of light on reactions

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Understand meaning of reaction rate.
2. Compute the average and instantaneous rate of chemical reactions either from the slope of a tangent to a concentration vs time graph or by calculation.
3. Understand ways to measure reaction rates.
4. Determine rate expressions for a reaction from the initial concentrations of the reactants.
5. Calculate life-time, half-life time of a reaction.
6. Discuss the effect of reagents nature and concentration on reaction rate.
7. Calculate order of reaction
8. Differentiate order of reaction and molecularity of reaction.
9. Describe the temperature influence on reaction rate.
10. Discuss the collision theory of reactions, stating the factors that affect collision frequency.
11. Describe a reaction in terms of energy barrier, activated complex and threshold energy.
12. Distinguish between activation energy and threshold energy.
13. Discuss the role played by a catalyst in changing the path of a reaction.
14. Discuss the effect of light on chemical reactions.

11.1 INTRODUCTION

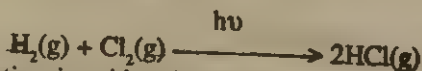
There are two basic questions in physical chemistry :

- (i) Where are chemical reactions going ?
- (ii) How fast are they getting there ?

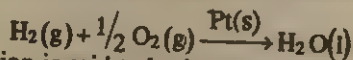
The first question can easily be answered by measuring the energy difference between the reactants and the products. The study of chemical equilibrium enables us to understand the extent to which a chemical reaction takes place. A high value of the equilibrium constant of a reaction indicates that the reaction is going to almost completion. However, the studies of free energy changes or chemical equilibrium are concerned with the initial and the final states of the system. They are quite silent about (i) what happens in the course of reaction i.e., reaction mechanism and (ii) the time that a reaction takes in going to a certain extent. We can conclude that there is no correlation between the rate of a reaction and its equilibrium constant.

To answer the second question, i.e., how fast a reaction will occur and what path will be followed by the reactants before they get converted into products, we must get ourselves familiar with the principles of **chemical kinetics**. These principles are the subject of this unit. In this unit we shall discuss the factors which actually determine and control the rate of chemical reactions and the mechanism by which chemical reactions occur. A number of factors govern the speed of a reaction. Experiments show that four important factors generally influence the rate of reaction : (i) nature of the reactants, (ii) concentration of the reactants (iii) temperature, and (iv) catalysts.

The number of phases for the reaction mixture is of immense concern in reaction rate studies. If only one phase occurs throughout as in the combination of hydrogen and chlorine to form hydrogen chloride gas,



the reaction is said to be *homogeneous*. If more than one phase is involved in the reaction, e.g., the formation of water from hydrogen and oxygen in the presence of platinum

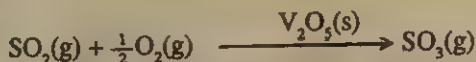


the reaction is said to be *heterogeneous*.

Exercise 11.1 : Indicate whether the following systems are homogeneous or heterogeneous.

- (i) a sugar solution in water
- (ii) muddy water
- (iii) silver coin
- (iv) concrete

(v) Contact process



Solution :

Homogeneous systems : (i) and (iii)

Heterogeneous systems (ii), (iv) and (v)

11.2 FEASIBILITY OF A REACTION

We know a chemical reaction takes place spontaneously if there is a decrease in its free energy, i.e., ΔG is less than zero. Consider the combination of silver nitrate with sodium chloride in aqueous solutions to form silver chloride,



It is a spontaneous reaction, but we observe that silver nitrate and sodium chloride aqueous solutions taken in two separate test tubes do not react to give silver chloride precipitate no matter how close the two test tubes are brought. Thus, apart from energetically feasible, a chemical change will take place when the reactants are brought in contact with each other. As we observe, a road accident occurs only when a pedestrian, a cyclist, a scooterist or a car collide with one another. Similarly a chemical change takes place when reacting molecules come in contact of each other and collide among themselves.

11.3 RATE OF REACTION

11.3.1 Meaning of Reaction Rate

Reactions proceed at different rates. Let us see what the expression "the rate of a reaction" means. Consider the reaction between carbon monoxide, CO, and nitrogen dioxide.

Experiment 11.1 : Take 0.1 mole each of carbon monoxide and nitrogen dioxide in a 2 litre closed flask and observe the colour of the mixture. Now place the flask in an oil bath heated to 500K. Watch the change in colour with time.

Observation : We observe that initially the gaseous mixture is dark brown in colour Fig. 11.1(a). When the flask is kept in oil bath heated to

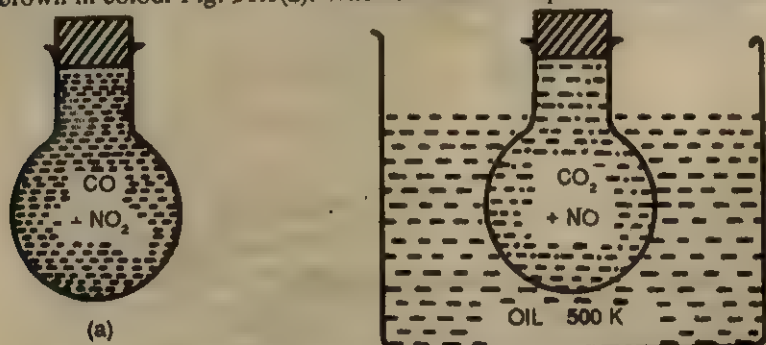


Fig. 11.1 Reaction mixture : CO and NO₂ at two different temperatures : (i) room temperature, and (ii) 500K

500K, there is a gradual disappearance of the reddish brown colour with time.

Inference : Reaction : $\text{CO} + \text{NO}_2 \longrightarrow \text{CO}_2 + \text{NO}$

is taking place. Since the other gases are colourless, the colour change indicates the number of moles of NO_2 that have reacted during the time interval. The quotient of number of moles reacted divided by time interval, is called the rate of the reaction :

$$\begin{aligned}\text{Rate} &= \frac{\text{quantity of NO}_2 \text{ consumed}}{\text{time interval}} \\ &= \text{quantity of NO}_2 \text{ consumed per unit time}\end{aligned}$$

We observe it is not only the NO_2 but also CO which is consumed. Thus, we can express the rate of the reaction in terms of the rate of consumption of either CO or NO_2 . As CO and NO_2 are consumed, simultaneously CO_2 and NO are being formed. Equally well, we can express the rate of this reaction in terms of the appearance of either product CO_2 or NO . Which is to be used, depends on the one which is convenient to measure. If it is convenient to measure the production of CO_2 , we can express the rate in the form

$$\begin{aligned}\text{Rate} &= \frac{\text{quantity of CO}_2 \text{ produced}}{\text{time interval}} \\ &= \text{quantity of CO}_2 \text{ produced per unit time}\end{aligned}$$

Thus "the rate of a chemical reaction is the change per unit time of the concentration of either reactants or products in the reaction".

When we plot these concentration with time, a graph (Fig. 11.2) is obtained. An inspection of the curve reveals that the rate of this reaction changes with time.

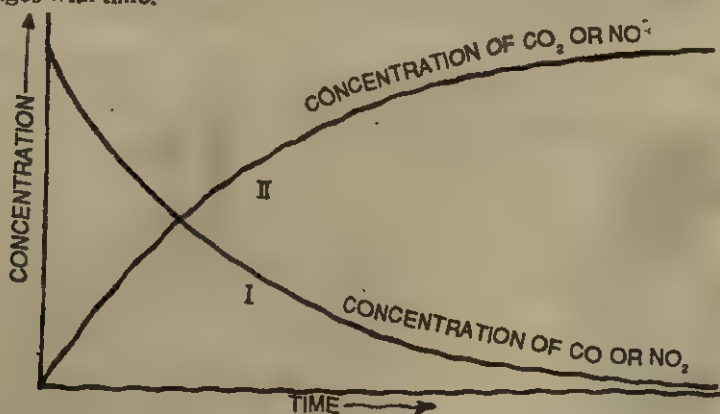


Fig. 11.2 Change in concentration of reactants and products with time

It can be seen from these curves, that at the start of the reaction, the concentration of either reactant is quite high which decreases rapidly with time (Fig. 11.2 curve-I). On the other hand, the concentration of

products which was nil in the beginning of the reaction increases quite fast with time (Fig. 11.2 curve II).

In general, the rate (or speed) of any chemical reaction can be expressed as the ratio of the change in concentration of a reactant (or product) to time interval.

Mathematically,

$$\text{Rate} = \frac{\text{final concentration of reactant} - \text{initial concentration of reactant}}{\text{time interval}} \quad \dots (11.1)$$

$$= \frac{\text{final concentration of product} - \text{initial concentration of product}}{\text{time interval}} \quad \dots (11.2)$$

$$= \frac{C_f - C_i}{\text{time interval}} \quad \dots (11.3)$$

here, C_f and C_i are the final and initial concentrations respectively (either reactant or product).

Now let us consider a simple reaction



i.e., reactant, R, changes into product, P, the rate of this reaction can be calculated by substituting the concentration of either R or P at different times in the equation 11.3. On substituting these values in equation 11.3, we get

$$\text{Rate} = \frac{[R]_f - [R]_i}{\text{time interval}} = - \frac{\Delta [R]}{\Delta t} \quad \dots (11.4)$$

$$\text{or Rate} = \frac{[P]_f - [P]_i}{\text{time interval}} = \frac{\Delta [P]}{\Delta t} \quad \dots (11.5)$$

On substituting the experimental values (the rate of reaction is always determined experimentally) of the concentration, we find that the rate as calculated from equation 11.4 comes out to be negative. The rate of a reaction is always positive. Thus, whenever the rate is expressed in terms of the concentration of reactants, a minus sign is always put before the expression. This minus sign is because the concentration of reactant decreases with time. Thus, the correct expressions for expressing the rate of a reaction are

$$\text{Rate} = - \frac{\Delta [\text{reactant}]}{\Delta t} \quad \dots (11.6)$$

$$\text{or Rate} = + \frac{\Delta [\text{product}]}{\Delta t} \quad \dots (11.7)$$

Consider a general reaction : $A + 2B \longrightarrow C + 2D$

The rate of this hypothetical or any other reaction can be expressed more specifically as the rate at which one of the reactants disappears or a product appears. Mathematically the rate can be written as,

$$\text{The rate of disappearance of the reactant, A} = - \frac{\Delta [A]}{\Delta t} \quad \dots (11.8).$$

Similarly if the rate of reaction is expressed as disappearance of reactant B, the rate could be

$$\text{Rate} = - \frac{\Delta [B]}{\Delta t} \quad \dots (11.9)$$

Since two moles of B react with one mole of A, thus, concentration of B which disappears in a certain period of time would be just the double of the concentration of the reactant, A, which disappears in the same period of time. Thus, the correct expressions for the rate of this reaction are

$$\text{Rate} = -\frac{\Delta [A]}{\Delta t} = -\frac{1}{2} \frac{\Delta [B]}{\Delta t} \quad \dots\dots(11.10)$$

In a similar fashion one can write for the products :

$$\text{Rate} = \frac{\Delta [C]}{\Delta t} = \frac{1}{2} \frac{\Delta [D]}{\Delta t} \quad \dots (11.11)$$

where $\Delta [C]$ and $\Delta [D]$ represent the change in molar concentrations of products C and D respectively during the time interval Δt . The positive sign in the above expression denotes that $[C]$ and $[D]$ increased as time passed. From equations (11.10) and (11.11), we can express the rate of reaction :

$$\text{Rate} = -\frac{\Delta [A]}{\Delta t} = -\frac{1}{2} \frac{\Delta [B]}{\Delta t} = \frac{\Delta [C]}{\Delta t} = \frac{1}{2} \frac{\Delta [D]}{\Delta t} \quad \dots\dots (11.12)$$

The general way in which the rate of a reaction can be expressed is the quotient of concentration change with time, divided by the coefficient of that particular species in the balanced chemical equation. The minus sign is given in the equation if the rate is expressed as the change in the concentration of reactant, and plus sign is given in the equation when the concentration change of either product is considered.

Exercise 11.2 : For the reaction : $2\text{NO}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$ write rate expressions in terms of each chemical species.

Solution : Rate expressions for this reaction considering the concentrations of reactants and products are .

$$\text{Rate} = -\frac{1}{2} \frac{\Delta [\text{NO}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta [\text{NO}]}{\Delta t} = \frac{\Delta [\text{O}_2]}{\Delta t}$$

11.3.2 Units of Reaction Rate

Reaction rate has units of concentration divided by time. Concentration is expressed in moles per litre, time may be expressed in seconds, minutes, hours, days or years. Thus, the units of reaction rate would be

$$\frac{\text{mol}}{\text{L s}} \quad \frac{\text{mol}}{\text{L min}} \quad \frac{\text{mol}}{\text{L hr}} \quad \frac{\text{mol}}{\text{L yr}}$$

Concentration unit mol is convenient if the reaction is carried out in solution, but for a gaseous phase reaction the quantity consumed or produced is conveniently measured in partial pressure units.

11.3.3 Ways to Measure Reaction Rate

To determine the rate of a reaction, the change in the concentration of either reactant or product is measured with time. To measure the concentration at any instant, first the reaction is to be stopped which is done by pouring the reaction mixture in ice cold water. At this low temperature the rate of reaction is so low that it can be assumed to be almost stopped. This process is called

freezing the reaction'.

Reaction rates are determined by measuring the rate at which some property of the reaction changes. Some important properties which have been studied are colour, volume of the system, pressure, rotation of polarized light, weight of reactant consumed or precipitate formed, and p^H . The examples in Table 11.1 illustrate how some of these properties are used.

TABLE 11.1 : Illustrative examples of properties used to determine the concentration.

S.No.	Property which changes with time	Sample reaction
(i)	Colour	$N_2O_5(g) \rightarrow 2NO_2(g)$
(ii)	Volume/pressure	$N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2} O_2(g)$ $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
(iii)	Rotation of polarized light	Inversion of sucrose $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$ Sucrose Glucose Fructose
(iv)	Weight	$Zn(s) + 2HCl(l) \rightarrow ZnCl_2(aq) + H_2(g)$
(v)	p^H	$CH_3COOC_2H_5(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + C_2H_5OH(aq)$

11.3.4 Average Rate of Reaction

The rate of a reaction over a time interval is usually referred to as average rate of a reaction. It can be determined as follows.

$$\text{Rate} = - \frac{[\text{reactant}]_f - [\text{reactant}]_i}{\text{time interval}}$$

$$\text{or Rate} = \frac{[\text{product}]_f - [\text{product}]_i}{\text{time interval}}$$

Exercise 11.3 : If it takes 1 nanosecond for hydrogen ions concentration of $1 \times 10^{-3} \text{ M}$ to disappear, what is the average rate of the reaction ?

Solution :

$$\begin{aligned} \text{Rate} &= \frac{\text{concentration change}}{\text{time}} \\ &= \frac{1 \times 10^{-3} \text{ mol L}^{-1}}{1 \times 10^{-9}} \\ &= 1 \times 10^6 \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

Exercise 11.4 : In a given reaction : $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ at 400K it is observed that the oxygen pressure falls from 0.50 to 0.10 atm in 30 min. Calculate the average rate of reaction in (i) atmospheres per minute and (ii) molarity per second.

Solution : (i)

$$\begin{aligned} \text{Rate} &= - \frac{\text{change in partial pressure}}{\text{time}} \\ &= - \frac{0.10 - 0.50 \text{ atm}}{30 \text{ min}} \end{aligned}$$

$$= \frac{0.40 \text{ atm}}{30 \text{ min}} = 0.0133 \text{ atm/min}$$

(ii) For an ideal gas, $PV = nRT$ or $F = \frac{nRT}{V} = CRT$ or $C = \frac{P}{RT}$ thus, concentration in moles per litre $\frac{n}{V}$ is equal to P (atm) divided by RT

$$\begin{aligned} \text{Rate} &= \frac{0.0133 \text{ atm/min} \times 1 \text{ min/60 s}}{0.082 \text{ litre atm mol}^{-1} \text{ deg}^{-1} \times 400 \text{ deg}} \\ &= 6.76 \times 10^{-6} \text{ M s}^{-1} \end{aligned}$$

Exercise 11.5 For a reaction following data was obtained,

(R) (mol/L)	2.0	1.8	1.5	1.3	1.1	0.9
Time (s)	0	5	20	30	50	80

calculate average rate of reaction (i) upto 5 seconds and (ii) between 20 and 30 seconds.

Solution : Average rate of reaction between 0 and 5 seconds

$$\begin{aligned} &= \frac{1.8 - 2.0}{5} \\ &= 0.04 \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

(ii) Average rate of reaction between 20 to 30s interval

$$= \frac{1.3 - 1.5}{30 - 20} = \frac{0.2}{10} = 0.02 \text{ mol L}^{-1} \text{ s}^{-1}$$

The average rate over a very small time interval can be determined with the help of concentration vs time curve (Fig. 11.3). If we

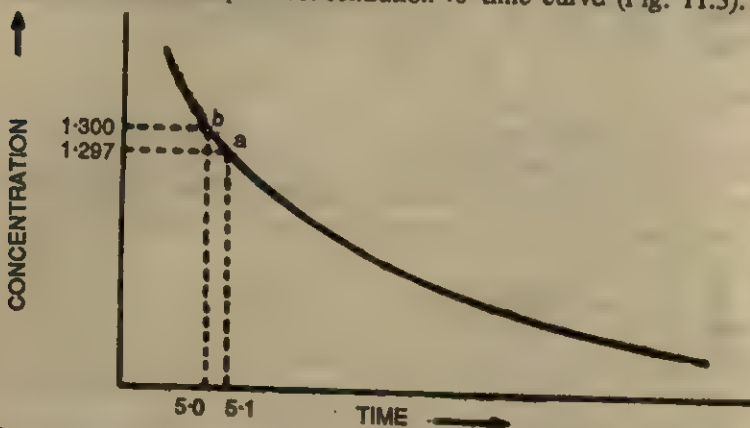


Fig. 11.3 Determination of the average rate of reaction for a very short time interval

want to know average rate between 5 and 5.1 s interval, we shall draw two perpendicular lines from these time points at abscissa. Let these lines touch the curve at point a and b. Now draw two perpendicular lines from a and b on coordinate axis. Let the values be as shown on the axis. Now

$$\text{Rate} = \frac{1.297 - 1.300}{5.1 - 5}$$

$$\text{or } = \frac{0.003}{0.1} = 0.03 \text{ mol L}^{-1} \text{ s}^{-1}$$

11.3.5 Determination of Instantaneous Rate

The instantaneous rate of a reaction is also estimated with the help of concentration vs time curve (Fig. 11.4). It is the slope of a tangent line at the time at which the instantaneous rate is required.

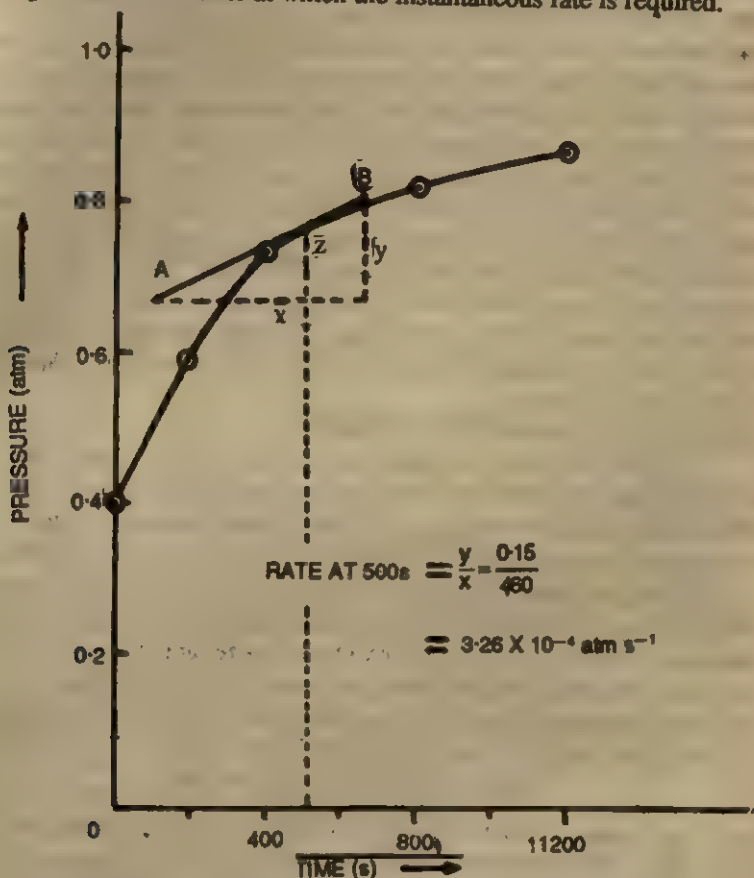


Fig. 11.4 Estimation of the instantaneous rate of the reaction.

Exercise 11.6 : Dissociation of hydrogen iodide is studied by measuring the total pressure p in the reaction vessel

time (s)	0	200	400	800	1200
p (atm)	0.40	0.58	0.74	0.82	0.86

calculate the rate of the reaction after 500 seconds from the start of the reaction.

Solution : Plot a graph between pressure vs time (Fig. 11.4). Draw a perpendicular line to the curve from the point 500 s on the time axis. Let this perpendicular line meet the curve at the point Z. From Z, draw a tangent AB on the curve, slope of this tangent is the rate of the

reaction at 500 s.

Rate of reaction at 500s = slope of tangent AB = $\frac{y}{x} = 3.26 \times 10^{-4} \text{ atm s}^{-1}$

11.3.6 Time Dependence of Reaction Rate

From the slope of the tangents at various points on the concentration vs time curve (Fig. 11.4) it can be seen that the rate of reaction is not constant but decreases as the reactants are consumed. This decrease is very fast in the beginning of the reaction but slows down as time passes. Since the reaction rate is not constant it is essential to specify the concentration as well as the temperature when considering rate of a reaction. To compare the rate of two or more reactions we can specify concentrations of reactants (say 1 mol L^{-1}) for all the reactants and compare the time it takes for converting a definite portion of reactants into products. Usually when 98% reactants are converted into products, the time taken by the reaction is called **LIFE TIME**. The shorter the reaction life-time, the faster is the reaction. It is more convenient to compare the time for 50% completion. The time required by a reaction to get 50% of its reactant(s) converted into product(s) is called **half life-time** and is denoted by $t_{1/2}$.

11.4 SLOW AND FAST REACTIONS

On the basis of the rate, a chemical reaction may be termed as slow or fast reaction. If rate of reaction is so high that the time for completion of reaction cannot be measured with the help of common watches the reaction will be known as fast reaction. Most ionic reactions are fast reactions.

There are several reactions which take several days, months or years for their completion. These reactions are usually referred to slow reactions. In between the two extremes, there are several reactions which can be easily studied in the laboratory for a few seconds to several hours duration. These reactions are referred to moderate reactions. The reactions with their times for completion are given in Table 11.2.

TABLE 11.2 Reactions with their life-time

(i)	Fast reactions	Time for completion
	$\text{NaCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{NaNO}_3$	10^{-10} s
	$2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4$	10^{-12} s
	$\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$	1 ns
	$^{210}\text{Po} \rightarrow ^{210}\text{Pb}_{82} + ^4_2\text{He}$	$1.5 \times 10^{-13} \text{ s}$
(ii)	Moderate reactions	
	$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}_2\text{O} + \text{CO}_2$	5 min
	$\text{N}_2\text{O}_5 \xrightarrow{330\text{K}} 2\text{NO}_2 + \frac{1}{2}\text{O}_2$	8 hr
	$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow[310\text{K}]{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$	12 hr
(iii)	Slow reactions	
	$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$	30 yr
	$^{232}\text{U}_{92} \xrightarrow{\alpha} ^{228}\text{Th}_{90}$	$4.5 \times 10^{10} \text{ yr}$
	$\text{Cr}(\text{H}_2\text{O})_6^{3+} + \text{I}^- \rightarrow \text{Cr}(\text{H}_2\text{O})_5\text{I}^{2+} + \text{H}_2\text{O}$	$2 \times 10^4 \text{ yr}$

Exercise 11.7 : Select the member of each pair having the greater reaction rate. Assume similar conditions within each pair.

- (i) Evaporation of water or evaporation of gasoline
- (ii) Paper burning or candle burning
- (iii) Iron rusting or copper tarnishing

Solution :

- (i) Gasoline evaporates faster than water
- (ii) Paper burns faster than candle
- (iii) Iron rusts faster than copper tarnishes.

11.5 FACTORS AFFECTING RATE OF REACTION

In section 11.3.5 we have seen that reactions move with different speeds. Here, we shall discuss factors which affect the rate of a reaction. The basic factors which are considered here are (i) nature of the reactants, (ii) the concentration, (iii) the temperature and (iv) the catalyst.

11.5.1 The Nature of the Reactants

Consider the following three reactions, all of which occur in aqueous solutions.

- (i) $5\text{C}_2\text{O}_4^{2-}(\text{aq}) + 2\text{MnO}_4^{-}(\text{aq}) + 16\text{H}^{+}(\text{aq}) \longrightarrow 10\text{CO}_2(\text{g}) + 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O}(\text{slow})$
- (ii) $5\text{Fe}^{2+}(\text{aq}) + \text{MnO}_4^{-}(\text{aq}) + 8\text{H}^{+}(\text{aq}) \longrightarrow 5\text{Fe}^{3+}(\text{aq}) + \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{Very Fast})$
- (iii) $\text{Ag}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq}) \longrightarrow \text{AgCl}(\text{s})$ (instantaneous)

Potassium permanganate solution is decolourized by both $\text{C}_2\text{O}_4^{2-}$ ions as well as Fe^{2+} . Yet, the time required for the decolourization is quite different. The third reaction takes place instantaneously and that too to almost completion.

Though all the three are ionic reactions, yet their rates are quite different. The difference lies in the specific characteristics of these ions. The conversion of ions to another ionic species is quite fast while the conversion of ions, $\text{C}_2\text{O}_4^{2-}$, to molecular species, CO_2 , is slow. On the basis of experimental observations, following rules can be framed.

1. Reactions that do not involve bond rearrangement are usually rapid at room temperature.
2. Reactions in which bonds have to be broken and some new bonds have to be formed are usually slow at room temperature.

Exercise 11.8 : Identify the given reactions likely to be extremely rapid, moderate or slow at room temperature.

- (i) $\text{Cr}^{2+}(\text{aq}) + \text{Fe}^{3+}(\text{aq}) \longrightarrow \text{Cr}^{3+}(\text{aq}) + \text{Fe}^{2+}(\text{aq})$
- (ii) $3\text{Fe}^{2+}(\text{aq}) + \text{NO}_3^{-}(\text{aq}) + 4\text{H}^{+}(\text{aq}) \longrightarrow 3\text{Fe}^{3+}(\text{aq}) + \text{NO}(\text{g}) + 2\text{H}_2\text{O}$
- (iii) $\text{C}_8\text{H}_{18} + 12\frac{1}{2}\text{O}_2 \longrightarrow 8\text{CO}_2(\text{g}) + 9\text{H}_2\text{O}(\text{g})$

Solution : Reaction (i) is very rapid. It involves only ionic species and does not involve bond breaking of a large number of ions.

Reaction (ii) seems to go with moderate rate or slow as it involves bond breaking as well as large number of ions.

Reaction (iii) will be very very slow, in fact at room temperature there is no reaction. It involves many bonds to break and to form.

11.5.2 Factors affecting the number of collisions between the reactant molecules

In the molecular model of matter, two molecules must collide to undergo a chemical reaction. Thus, factors which can increase the number of collisions per unit time would increase the rate of the reaction. The following two factors affect the collision frequency.*

(i) Concentration of reactants

The following experiment demonstrates the effect of concentration on reaction rate.

Experiment 11.2 : Take dilute solutions of hydrochloric acid and sodium thiosulphate (Hypo). Add 1, 2, 3, 4 and 5 cm³ 0.1 M hypo solution in five different test tubes numbered 1, 2, 3, 4 and 5. Make volume of solution in each test tube to 5 cm³ by adding 4, 3, 2, 1, 2, 1 and 0 cm³ in test tubes numbered 1, 2, 3, 4 and 5 respectively.

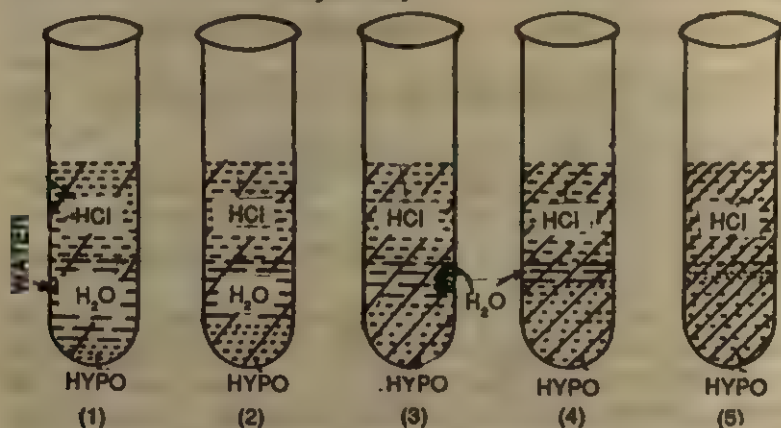
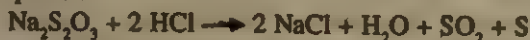


Fig. 11.5 Concentration effect on reaction rate

Now add 5 ml HCl solution in all the test tubes. The following reaction will take place :



The precipitation of sulphur can be observed in the form of a white turbidity in the solution. Note down the time for the just appearance of white turbidity in these test tubes. You will observe that time is minimum for test tube numbered 5 and maximum for test tube numbered 1.

Inference : As we know that the concentration of hypo is minimum in test tube 5, the time taken is inversely proportional to the concentration. As rate is inversely proportional to time for the completion of reaction.

* Collision frequency is the number of collisions occurring between molecules in a unit volume in the unit time

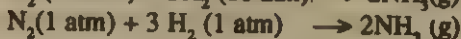
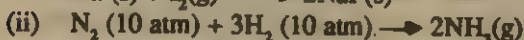
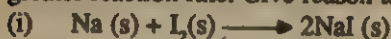
one can conclude that the rate of reaction will increase with increase in the concentration of reactants.

Increase in the concentration brings reacting species - atoms, molecules, or ions closer thereby increases the number of collisions in unit time.



Fig. 11.6 Number of collisions depends upon the concentration

Exercise 11.9 : Select the reaction of each reaction pair having the greater reaction rate. Give reason to support your answer -



Solution :

(i) $\text{Na(s)} + \text{I}_2\text{(g)}$ reaction is faster because collisions will be more frequently possible in gas and solid species, than solid and solid species.

(ii) $\text{N}_2\text{ (10 atm)} + 3\text{H}_2\text{ (10 atm)} \longrightarrow 2\text{NH}_3\text{(g)}$ would have much faster rate than that of the two gases at 1 atm pressure because the number of molecules per unit volume are much larger at higher pressure thereby increasing the number of collisions among them, this way increasing the rate of the reaction.

Does rate of reaction depend on the external pressure ? In case of solid and liquid-phase reactions, the increase in pressure hardly brings any change to rate of chemical reaction. However, in gaseous reactions the increase in pressure decreases the volume, thereby increases the concentration of reacting molecules per unit volume, the rate of reaction is also increased. But the increase in rate of reactions with increase in pressure should be understood as due to increase in the concentration of reacting substances. As such, pressure does not change the rate of reaction.

(ii) Surface Area or State of Aggregation

Reacting substances may exist in solid, liquid or gas phase. The state of reacting substances also influences the rate of reaction.

Experiment 11.3 Take two test tubes a and b. In test tube 'a' put one piece of chalk (CaCO_3) weighing 1.0 g. In the test tube 'b' put 1.0 g powdered chalk (Fig. 11.7). Now add 5 cm³ dil HCl in both the test

tubes and note the effervescence.

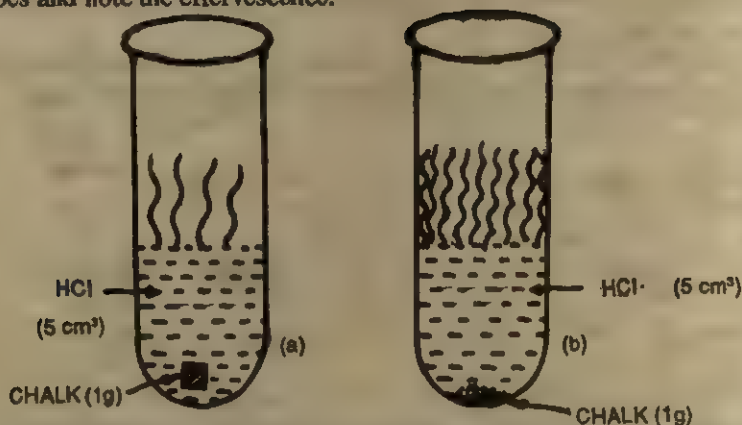


Fig. 11.7 : Reaction between chalk (in two different states of subdivision) and dil. HCl.

It is observed that in the test tube *b* the effervescence is quite vigorous.

Experiment 11.4 : Take 10g sugar, powder it and place it in one beaker. In another beaker, place 10 g crystals of sugar. Add 100 cm³ water in both the beakers and stir. Observe the time in which sugar completely dissolves. It is observed that powdered sugar disappears soon while crystals of sugar take longer time to disappear.

Let us examine what happens when substances are divided into fine particles. Consider a cube of 5 cm side. The volume of this cube will be 125 cm³ and surface area will be $6 \times 5 \times 5 = 150 \text{ cm}^2$. When this cube is brought in contact of a reactant like HCl or H₂O, the molecules of these collide with the molecules on the surface of the cube. Thus, the number of collision will be dependent on the number of molecules at the surface. **More is surface area, more collisions will take place.** Now divide the cube in smaller cubes of 1 cm side. There will be 125 such cubes from the bigger cube. The surface area of each cube will be 6 cm² and so the total surface area of smaller cubes will be $6 \times 125 = 750 \text{ cm}^2$ i.e. 5 times more than the surface area of bigger cube (side 5 cm). The number of molecules at this surface will be more and the collisions will also be more. This will increase the rate of reaction.

To sum up, the rate of a reaction depends upon the rate with which molecules of reactants collide with one another. In the following ways the rate of reactions can be increased :

1. Stirring, mixing or dissolving two reactants.
2. In the solution increasing the concentrations of reactants, in gaseous phase increase in partial pressures of reacting gases.
3. Increasing the area of contact between the two reactants.

Yet we know there are certain reactions the rates of which do not

depend upon the concentration of reactants, this can be explained on the basis of reaction mechanism.

Exercise 11.10 : Which burns faster in air

- (i) a log of wood or wood splinters
- (ii) liquid gasoline or gasoline gas

Solution : (i) Splinters burn faster because the exposed surface is increased by peeling the wood.

(ii) Gasoline gas burns almost explosively because of increased surface area.

Exercise 11.11 : Explain why there is a danger of explosion where a large amount of dry, powdered, combustible material is stored.

Solution : Material when in the powdered form, the surface area is tremendously increased which offers many more possibilities of collision between the molecules of the material and air. The rate of reaction goes up increasing the chances of explosion.

Exercise 11.12 : Consider two gases A and B in a 1 litre flask at 300K. How the rate of reaction between these two gases be affected if the partial pressure of each gas inside the flask is doubled ?

Solution : Increase in partial pressure increases the concentration of both the reactants and consequently increases rate.

11.6 THE QUANTITATIVE EFFECT OF CONCENTRATION - THE ORDER OF A REACTION

It is found experimentally that the rate of a reaction is some function of concentration of reactant. For a reaction involving a single reactant



the rate expression has the general form

$$\text{Rate} = k [A]^m \quad \dots (11.13)$$

The power to which the concentration of reactant A is raised in the rate expression is called the **Order of the reaction**. If m in equation 11.13 is zero, the reaction is called "zero order" if $m = 1$, the reaction is first order. Here, k is known as the **rate constant** or **specific reaction rate**, which is equal to the rate of the reaction when reactant concentration is unity.



$$\text{Rate} = k [A]^m [B]^n \quad \dots (11.14)$$

The power m describes the order of the reaction with respect to A and the order is n with respect to the reactant B. The overall order of this reaction is $(m + n)$.

The order of a reaction is always experimentally determined. It cannot be predicted theoretically. It is defined as "the sum of the powers to which the concentration (or pressure) terms are raised in order to determine the rate of the reaction."

Molecularity of A Reaction

It is defined as the number of atoms, ions or molecules taking part in each step leading to the chemical reaction. For a multiple step reac-

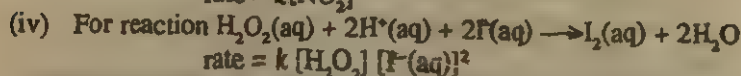
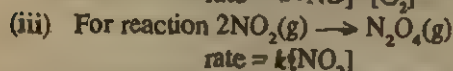
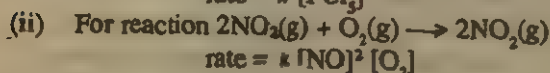
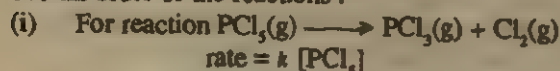
tion, overall molecularity is taken corresponding to rate determining step.

The differences between order and molecularity of a reaction are summarized in Table 11.3

TABLE 11.3 Differences between order and molecularity of a reaction

Order	Molecularity
(i) It is the sum of exponents of the molar concentration of the reactants in the rate equation.	It is the number of molecules of the reactant taking part in a single step chemical reaction.
(ii) It may or may not have relation with the stoichiometric equation for the reaction.	It is calculated from the reaction mechanism.
(iii) It depends on the experimentally determined rate for the overall reaction.	It depends on the rate determining step reaction in the reaction mechanism.
(iv) It may be a whole number or fractional.	It must always be a whole number.
(v) It is determined experimentally and cannot be obtained from a balanced chemical equation.	It is obtained from a single balanced rate determining step of chemical reaction.

Exercise 11.13 : The rate expressions for the following reactions are given below, find out the order with respect to each reactant and the overall order of the reactions :



Solution : The order with respect to a reacting species is the exponent of the concentration term of that species in the rate law expression. The overall order of the reaction is the sum of the powers to which the concentration terms of reacting species are raised in the rate expression. Thus, for reaction -

(i) order with respect to PCl_5 is one. One is also the overall order of this reaction.

(ii) in rate expression $[\text{NO}]$ is raised to 2 and $[\text{O}_2]$ is raised to 1. Thus the order with respect to $\text{NO}(\text{g})$ and $\text{O}_2(\text{g})$ are 2 and 1 respectively. The overall order of this reaction is $2 + 1 = 3$.

(iii) the order with respect to $\text{NO}_2(\text{g})$ as well as overall order of the reaction is one.

(iv) the order with respect to various reacting species is as follows :

Species	Order
$\text{H}_2\text{O}_2(\text{aq})$	one
$\text{H}^+(\text{aq})$	zero
$\text{I}^-(\text{aq})$	two

Overall order of this reaction is $1 + 0 + 2 = 3$

11.7 THE TEMPERATURE EFFECT ON REACTION RATE

Temperature has a pronounced effect on the rates of chemical reactions. Generally chemical reactions are accelerated by increase in temperature. The oxidation of iron or coal is very slow at ordinary temperatures but proceeds rapidly at high temperatures. In the decolourization of KMnO_4 with $\text{C}_2\text{O}_4^{2-}$ ions, heating is required but with Fe^{2+} ions no heating is required. The students in the laboratory generally use burner to enhance the rate of reactions. It is a well known fact that foods cook faster at higher temperatures than at lower ones.

Now it may be expected that as the temperature increases the collision frequency increases, leading to a faster reaction. This has been found true in practice but the reaction rate increases with temperature much faster than what can be explained by collision frequency. Collision frequency (which is proportional to \sqrt{T}) accounts for less than 1% of this increase. Clearly a rise in temperature of 100K can produce an enormous increase in the rate of a reaction.

We have seen in almost all the reactions that increasing the temperature has a very pronounced effect, always increasing the reaction rate. Two questions come to mind. These are :

1. Why does a temperature rise increase the rate of a reaction and
2. Why does a temperature increase have such a large affect ?

To answer these questions, we return to collision theory. Chemical reactions occur when colliding molecules possess a certain amount of energy called the **activation energy**. only those collisions which take place between the particles possessing energy equal to the activation energy are effective in bringing out the chemical reaction. A certain amount of energy called activation energy is to be possessed by these particles so that they can cross the energy barrier to be converted into products (Fig. 11.8).

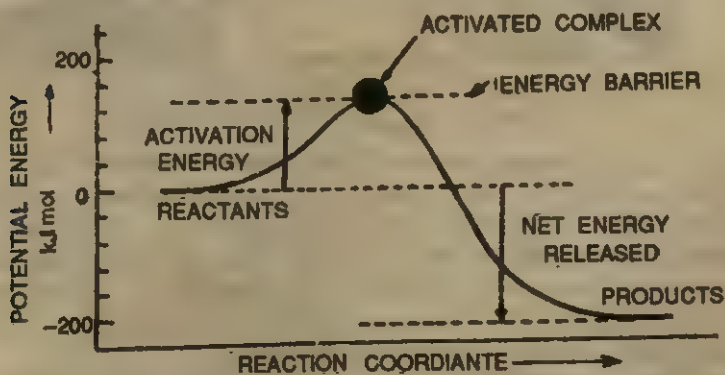


Fig. 11.8 Concept of energy barrier in chemical reaction

Activation energy of the reaction represents the minimum energy needed by a molecule (or a pair of molecules) to react. The activation

energy can be taken as minimum energy required by the molecules before they can overcome an energy barrier.

A small fraction of reactant molecules is only capable of overcoming the energy barrier. The fraction of such molecules increases with increase in reaction temperature. The rate of a chemical reaction depends on the product of collision frequency and the fraction of molecules which are in the activated state. Since only a small fraction of the molecules are activated, the rate of reaction is much smaller than the collision frequency. The higher the activation energy the smaller the fraction of activated molecules and the more slowly the reaction advances.

The possible fraction of the molecules having energies in excess or equal to any specific value (activation energy) can be found out from the Maxwell distribution of molecular kinetic curve at two different temperatures (Fig. 11.9). As the temperature increases the average en-

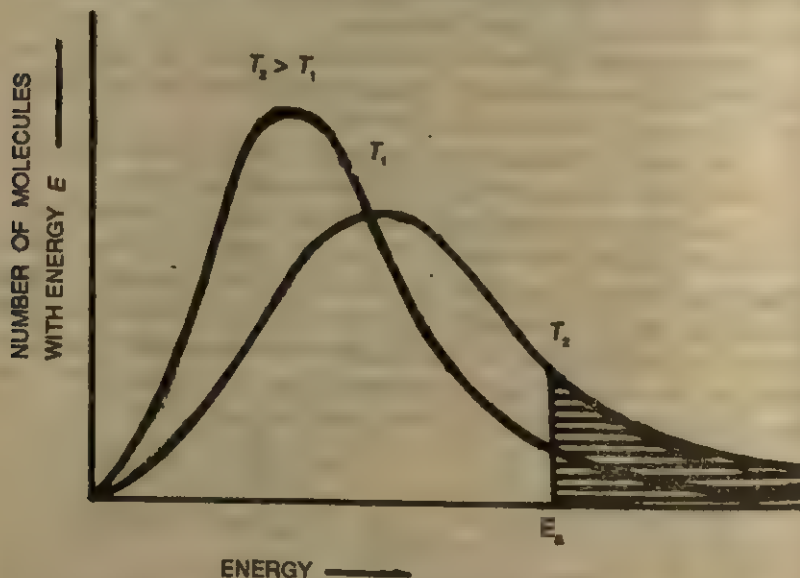


Fig. 11.9 Distribution of molecular energies at two temperatures. As temperature increases and the molecular energy distribution curve is shifted towards higher energies. The shaded region in Fig. 11.9 refers to the number of molecules with sufficient energy to react. Thus, it is clear that with increase in temperature the number of such molecules will increase and will decrease rapidly as E_a increases. Therefore, the reaction rate will be markedly increased by an increase in temperature.

11.7.1 Theory of Absolute Reaction Rate and Activation Energy (Transition State Theory)

There are certain reactions which can be considered to proceed via the formation of an activated complex as a result of collision be-

tween molecules possessing higher energy than the reactants and the products separately. There exists an equilibrium between reactant molecules and the activated complex. The complex can decompose either to give products or reactants.

Let us examine the formation of hydrogen iodide from hydrogen and iodine.



Accordingly, as a result of molecular interactions between the molecules of H_2 and I_2 the bonds present in the molecules get enlarged or loosened and an intermediate complex results.

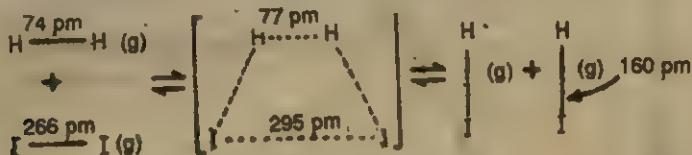


Fig. 11.10 Activated complex

This complex is highly unstable as it has higher energy. The complex decomposes very quickly either to form products or the parent reactants depending upon the conditions. The intermediate complex is termed as activated complex. Fig. 11.11 represents the energies involved in the reactants, the intermediate and the products. It is also known as energy profile.

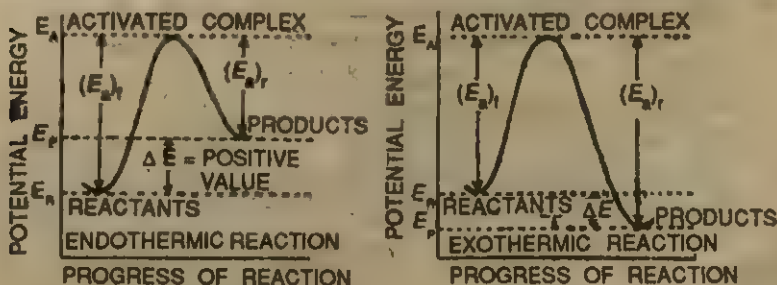


Fig. 11.11 Energy changes during a chemical reaction

Where E_a , E_r and E_p represent the energies of the activated complex, the reactants and the products respectively. $(E_a)_f$ and $(E_a)_r$ denote the energy of activation for the forward and reverse reactions and ΔE denotes the difference in energies of the products and the reactants.

Thus, for the reaction to occur, the reactants must acquire some energy, $E_a - E_r$. This is called the activation energy for the forward reaction, $(E_a)_f$. Similarly the activation energy for the reverse reaction would be equal to $E_a - E_p$ or $(E_a)_r$. Thus, the relationship between activation energy and the heat of reaction, ΔH , will be,

$$\Delta H = (E_a)_f - (E_a)_r$$

Exercise 11.14 : In a collision of molecules what is the main factor that determines whether a reaction will occur ?

Solution : The main factor is whether the molecules possess sufficient energy called the threshold energy to overcome the energy barrier.

Exercise 11.15 : Potential energy diagram for the reaction

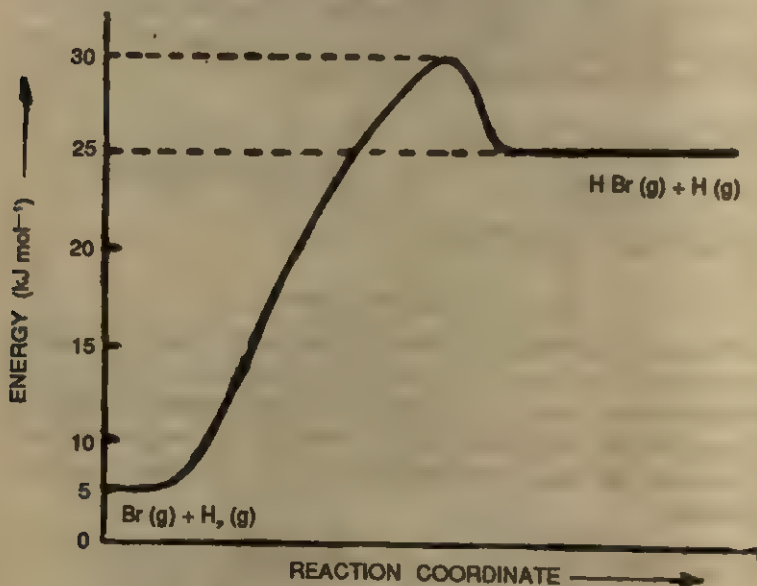
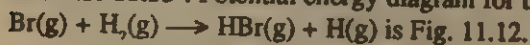


Fig. 11.12

- (i) What is the energy of activation, $(E_a)_f$, for the reaction $\text{Br(g)} + \text{H}_2(\text{g}) \longrightarrow \text{HBr(g)} + \text{H(g)}$
- (ii) What is the energy of activation $(E_a)_r$, for the reaction $\text{HBr(g)} + \text{H(g)} \longrightarrow \text{Br(g)} + \text{H}_2(\text{g})$
- (iii) What is the threshold energy of the reaction (i).

Solution :

- (i) $E = 25 \text{ kJ}$
- (ii) $E = 5 \text{ kJ}$
- (iii) Threshold energy = 30 kJ

11.8 CATALYSTS

Many reactions proceed quite slowly when the reactants are mixed alone but can be made to occur much more rapidly by the introduction of other substances. These substances are called catalysts and are not used up in the reaction. In a reversible reaction, a catalyst speeds up both the forward reaction and the backward reaction so that the equilibrium is established very soon. It does not disturb the equilibrium state at all.

When a catalyst is added, a new reaction path is opened up with a

different energy barrier (Fig. 11.13). The solid curve shows the activa-

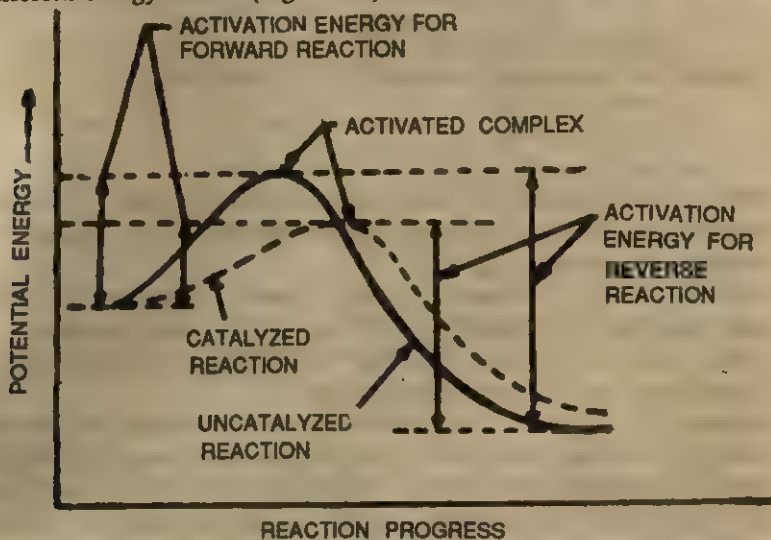


Fig. 11.13 Activation energy diagram for catalysed and non-catalysed reactions.

tion energy barrier which must be overcome for the reaction to occur. The new reaction path in presence of a catalyst is shown as a dotted curve. The catalysed route possesses a lower activation energy and a different activated complex. Thus, more reacting particles can get over the new lower energy barrier and the rate of reaction is increased.

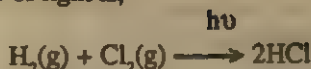
It is also clear that the activation energy for the reverse reaction is lowered exactly by the same amount as for the forward reaction. This explains why a catalyst has an equal effect on the reverse reaction. If a catalyst doubles the rate in one direction, it also doubles the rate in the reverse direction. The equilibrium is not disturbed but it is brought about in a shorter time.

The function of a catalyst is to split up the main reaction into two or more steps. The potential energy barrier for each step is smaller than that for the single step of the main reaction. In other words, the catalyst helps to cross the barrier in two or more steps.

11.9 EFFECT OF LIGHT ON REACTIONS

We know methane can be chlorinated in the presence of light. Toluene when reacts with chlorine in the presence of UV light forms benzyl chloride; photographic plate is effected by light, thus, there are many reactions which are photosensitive, such reactions are called photochemical reactions. In such reactions energy needed by the reacting molecules to overcome the energy barrier is supplied by light. These reactions usually proceed via the formation of free radicals. For example, the photochemical combination of hydrogen and chlorine in the

presence of light is,

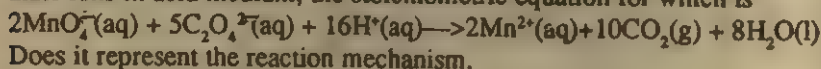


The reaction is considered to follow the following route



Thus, the free radical Cl^\bullet once formed by the absorption of light is regenerated. The chain continues until the reactants are exhausted or Cl^\bullet free radicals combine to give Cl_2 .

Exercise 11.16 : Consider the decolourization of permanganate by oxalate ions in acid medium, the stoichiometric equation for which is



Does it represent the reaction mechanism.

Solution : The answer is no. It is clear that the reaction does not take place in one step as represented by stoichiometric equation. There is remote probability that 23 species will orient themselves in such a way that they would collide simultaneously. Thus, a stoichiometric equation tells only the overall reaction, not the various steps which the reaction follows.

When a reaction takes place in more than one steps, it is the slowest step which determines the rate of reaction i.e., controls the kinetics of the reaction.

Dynamicity of chemical equilibrium

Chemical equilibrium is dynamic in nature has been discussed in Unit 9 of this book

SELF ASSESSMENT QUESTIONS

MULTIPLE CHOICE QUESTIONS

11.11 Put a (✓) mark against the most appropriate choice:

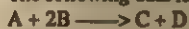
- (i) Which of the followings is a homogeneous system ?
 - (a) A pile of beans containing gravel
 - (b) Sugar solution in water
 - (c) Decomposition of $\text{PCl}_5(\text{s})$ into $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 - (d) Saturated solution of sodium chloride in water
- (ii) Which of the following factors does not affect reaction rate ?
 - (a) Concentration of reactants
 - (b) Temperature of reaction
 - (c) Size of solid reactant particles
 - (d) Total pressure in a gas phase reaction
- (iii) For the net reaction $2\text{X} + \text{Y} \longrightarrow \text{Z}$, the rate law for the formation of Z is :
 - (a) $r = k [\text{X}]^2 [\text{Y}]$
 - (b) $r = k [\text{X}] [\text{Y}]$
 - (c) $r = \frac{[\text{Z}]}{[\text{X}]^2 [\text{Y}]^2}$
 - (d) cannot tell from the above data
- (iv) Which of the following is a slow reaction ?
 - (a) $\text{Fe}^{3+} + \text{SCN}^- \longrightarrow \text{Fe}(\text{SCN})^{2+}$
 - (b) $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l})$
 - (c) $\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{CH}_3\text{COOH}(\text{aq}) + \text{C}_2\text{H}_5\text{OH}(\text{aq})$



(v) For the reaction $\text{SO}_2\text{Cl}_2(\text{g}) \longrightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ the expression for the rate law is $\text{rate} = k[\text{SO}_2\text{Cl}_2]$ the order of reactions is

(a) Zero (b) One (c) $\sqrt{2}$ (d) 2

(vi) The following data is obtained for the reaction



Experiment Number	Initial Molar Concentrations $\times 100$			Initial Rate Formation of D, Ms^{-1}
	[A]	[B]	[C]	
I	2.0	2.0	2.0	2.0
II	2.0	1.0	2.0	2.0
III	4.0	5.0	2.0	8.0

In experiment III, the rate (in Ms^{-1}) with which C appears is :

(a) 16.0 (b) 8.0 (c) 4.0 (d) 2.0

(vii) The unit for rate constant for the first order reaction is

(a) s^{-1} (b) Mol L^{-1} (c) $\text{Mol}^{-1} \text{L s}^{-1}$ (d) $\text{Mol}^{-1} \text{L s}^{-1}$

(viii) The reaction $\text{R} \longrightarrow \text{products}$, is a first order in R. If 2.4 g of R is allowed to decompose for 20 s, the mass of R remaining unchanged is found to be 0.60 g. What is the half-life, $t_{1/2}$ of this reaction ?

(a) 20 s (b) 10 s (c) 5 s (d) 1 s

(ix) A first order reaction

$\text{A} \longrightarrow \text{products}$, has a half-life of one hour. Whatever the quantity of substance A involved in the above reaction,

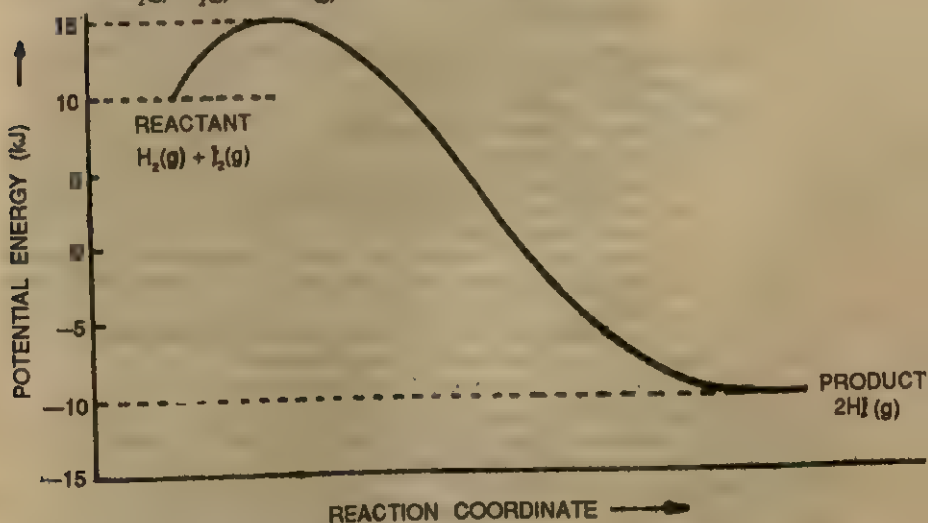
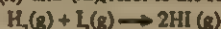
(a) the reaction goes to completion in 2 hrs

(b) the quantity of 'A' left after 2 hour is half the initial concentration of 'A'

(c) the concentration of 'A' left after 2 hour is $\frac{1}{4}$ th the initial concentration of A.

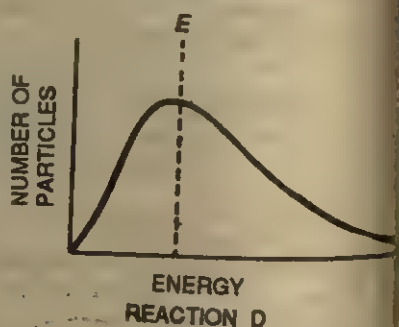
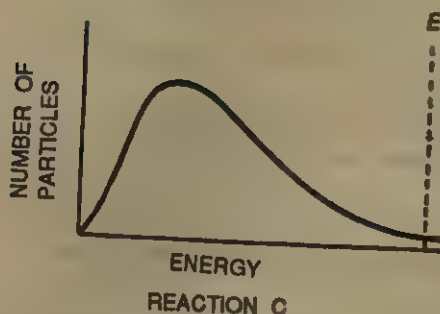
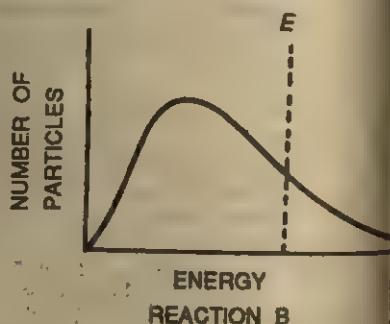
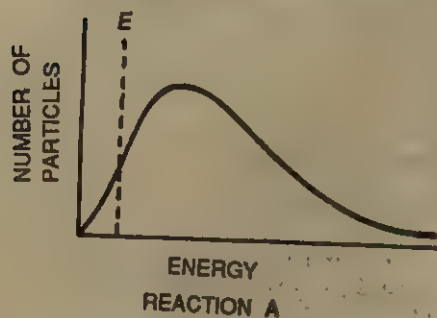
(d) The concentration of A left after 2 hours is $\frac{3}{4}$ th of the initial concentration of A.

Questions (x) and (xi) refer to the following potential energy diagram for the reaction



(x) The activation energy, E_a , for the reverse reaction $2\text{HI}(\text{g}) \longrightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ would be

- (a) 10 kJ (b) - 10 kJ (c) 20 kJ (d) 25 kJ
- (xi) The activation energy for the reaction could be
- decreased by increasing the initial concentration of C
 - decreased by a suitable catalyst
 - increased by decreasing the temperature
 - increased by increasing temperature
- (xii) Consider the following identical kinetic energy distribution curves for four different reactions all taking place at room temperature. Select the fastest reaction if only the threshold energy is different



- (xiii) The half-life period of radioactive element is 140 days. After 560 days, one gram of the element will reduce to

(a) 1/2 (b) 1/4 (c) 1/8 g (d) 1/16 g

(IIT 1986)

- (xiv) In a reaction, the threshold energy is equal to

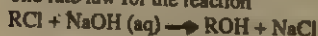
- activation energy
- activation energy + normal energy of reactants
- activation energy - normal energy of reactants
- normal energy of reactants.

- (xv) For a reaction $A + B \rightarrow \text{Products}$, the rate of the reaction was found to increase by 1.80 times when the temperature was raised by 273 K. A large increase in the rate of the reaction is due to

- increase in the number of collisions between reacting molecules
- lowering of the activation energy of the reactants
- increase in the activation energy of the reactants
- increase in the number of active molecules.

- 11.2 (i) Among the four answers given for each subquestion, one or more is correct. Write down all the correct answers.

The rate law for the reaction



is given by, rate = $k[\text{RCl}]$

The rate of the reaction will be

- (a) doubled on doubling the concentration of sodium hydroxide
- (b) halved on reducing the concentration of alkyl halide to one half
- (c) increased on increasing the temperature of the reaction
- (d) unaffected by increasing the temperature of the reaction. (IIT 1988)

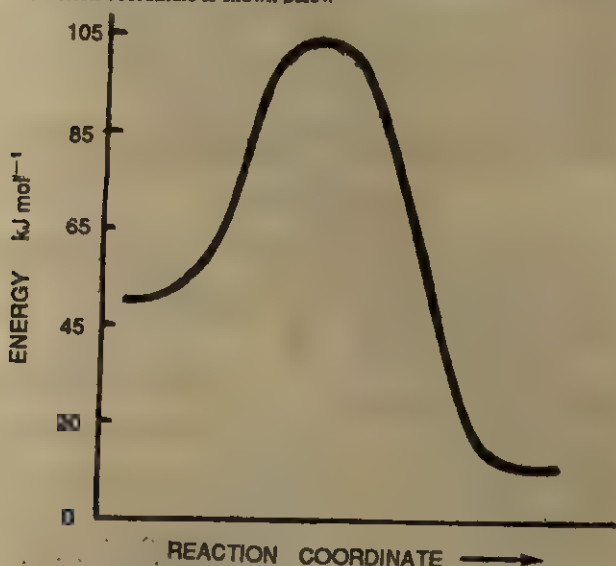
- (ii) A catalyst
 - (a) increases the average kinetic energy of reacting molecules
 - (b) decreases the activation energy
 - (c) increases the frequency of collisions of reacting species
 - (d) increases the rate of forward reaction as well as of reverse reaction.

11.3 Fill in the blanks :

- (i) If reactants and products are present in a single phase, the system is said to be _____
- (ii) The rate of a reaction is the quotient of decrease in concentration of reactant and _____
- (iii) If a reaction proceeds in such a way that its rate law is independent of the reactants concentration, the order of such reaction is _____
- (iv) For a _____ order reaction the half-life ($t_{1/2}$) is independent of the concentration of the reactant.
- (v) The rate constant, k , is the _____ in the rate law of a chemical reaction.
- (vi) The rate of a chemical reaction is a measure of the rate or speed with which a _____ disappears or a _____ appears.
- (vii) The function of a catalyst is to lower the _____ for a chemical reaction.
- (viii) The decomposition of hydrogen peroxide to water and oxygen

$$2\text{H}_2\text{O}_2(l) \longrightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$$
 is a first order reaction. The rate law for this reaction is _____
- (ix) The rate of the reaction

$$2\text{HI}(g) \longrightarrow \text{H}_2(g) + \text{I}_2(g)$$
 in terms of $\Delta[\text{HI}]$ is _____ so that the rate is the same as in terms of $\Delta[\text{H}_2]$.
- (x) In the reaction, Reactant \longrightarrow Product, the potential energy as a function of reaction coordinate is shown below



Indicate on the diagram the energy of the reactant, the product, the activation energy, and ΔH for the reaction.

11.4 Point out the correct statements of the following

- (i) Increasing the total pressure in a gas phase reaction increases the rate of reaction.
- (ii) Reactions with high activation energies are usually endothermic.
- (iii) For a reaction which takes place in more than one steps, the rate determining step is the slow one.
- (iv) The rate of a reaction does not change with time.
- (v) The rate of a catalysed reaction is always independent of the concentration of the catalyst.
- (vi) The rate constant for a reaction is independent of reactant concentrations.
- (vii) The energy necessary to cause a reaction between the colliding molecules is called the activation energy.
- (viii) Consider the following reaction pair
 - (i) $\text{C (s)} + \text{H}_2\text{O (g)} \xrightarrow{\text{catalyst}} 2\text{H}_2 \text{ (g)} + \text{CO}_2 \text{ (g)}$
 - (ii) $\text{C (s)} + \text{H}_2\text{O (s)} \xrightarrow{\quad\quad\quad} 2\text{H}_2 \text{ (g)} + \text{CO}_2 \text{ (g)}$
 The reaction (ii) is faster than the reaction (i)
- (ix) The decomposition of NO_2Cl involves the following two steps
 - $\text{NO}_2\text{Cl} \xrightarrow{\quad\quad\quad} \text{NO}_2 + \text{Cl} \text{ (slow)}$
 - $\text{Cl} + \text{Cl} \xrightarrow{\quad\quad\quad} \text{Cl}_2 \text{ (fast)}$
 - rate = $k [\text{NO}_2\text{Cl}] [\text{Cl}]$
- (x) A catalyst lowers the activation energy of the forward reaction as well as of reverse reaction to the same extent.

- 11.5 In the formation of ammonia by the Haber process,
 $\text{N}_2 \text{ (g)} + 3\text{H}_2 \text{ (g)} \rightleftharpoons 2\text{NH}_3 \text{ (g)}$,
 the rate of reaction was measured as $-\frac{\Delta[\text{N}]}{\Delta t} = 2.5 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$
 Express the rate in terms of $[\text{NH}_3]$.
- 11.6 The rate of disappearance of bromine in the hydrogen plus bromine reaction, which is of zero order, is given in units of moles per litre per second. What are the units for the specific rate constant
- 11.7 Draw an energy diagram to illustrate the energy relationships for an exothermic reaction.
- 11.8 Predict the overall order of a reaction for which half-life and units of rate constant do not depend on concentration.
- 11.9 The rate constant for a gaseous reaction is $6 \times 10^{22} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 298K. Express it in units of $\text{atm}^{-1} \text{ s}^{-1}$
- 11.10 Ammonia is made by passing nitrogen and hydrogen over an iron catalyst. Will the addition of iron speed up, or retard the decomposition of ammonia into its elements.

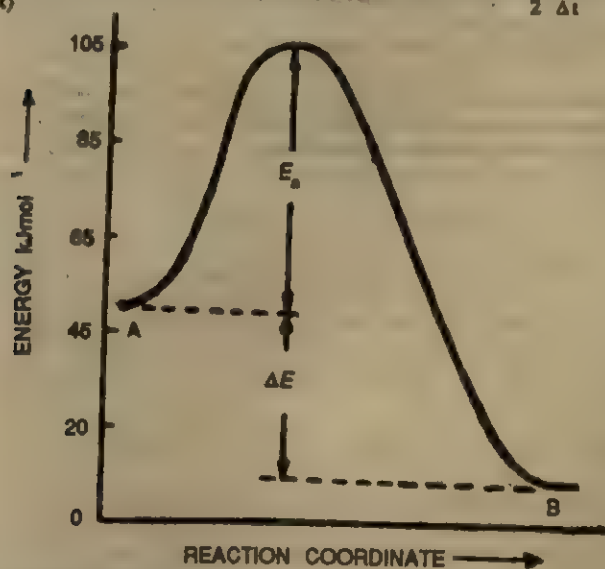
TERMINAL QUESTIONS

- 11.1 Pick the member of each pair having the greater reaction rate. Assume similar conditions.
- (a) Log of wood burning or splinters of wood burning
 - (i) $\text{CH}_3\text{CHO (g)} \xrightarrow{\quad\quad\quad} \text{CH}_4 \text{ (g)} + \text{CO (g)}$
 - (ii) $\text{CH}_3\text{CHO (l)} \xrightarrow{\quad\quad\quad} \text{CH}_4 \text{ (g)} + \text{CO (g)}$
- 11.2 Give three techniques that can be used to study the rate of a chemical reaction. Write four factors that affect the rate of a chemical reaction.
- 11.3 Why is the rate of reaction between $\text{H}_2 \text{ (g)}$ and $\text{Br}_2 \text{ (l)}$ more than that of between $\text{H}_2 \text{ (g)}$ and $\text{I}_2 \text{ (s)}$.
- 11.4 Why food cooks faster at high temperature than at lower temperature
- 11.5 Do you expect the reaction $\text{C}_6\text{H}_6 \text{ (l)} + \frac{15}{2} \text{O}_2 \text{ (g)} \rightarrow 6\text{CO}_2 \text{ (g)} + 3\text{H}_2\text{O (l)}$ to represent the mechanism by which benzene, C_6H_6 , burns. Why?
- 11.6 For a reaction
 $2\text{A} + \text{B} \rightarrow \text{C} + \text{D}$, if
 $-\frac{\Delta[\text{A}]}{\Delta t} = k [\text{A}]^2 [\text{B}]$.
- Write the rate of the reaction in terms of formation of C.

- 11.7 Phosphorous, P_4 , exposed to air burns spontaneously to give P_4O_{10} ; the ΔH of this reaction is $-2800 \text{ kJ per mole } P_4$. Draw an energy diagram for the net reaction, explaining the critical parts of the curve.
- 11.8 Why is it difficult to hard boil an egg at the top of 'China Peak', Nanital? Is it also difficult to cook scrambled eggs there. Explain.
- 11.9 An increase in temperature by 10°C does not double number of collisions between the molecules. Yet this temperature increase may double the rate of a slow reaction. Explain.
- 11.10 The rate at which CO is removed from the earth's atmosphere by bacteria in the soil is constant. What is the apparent order of this process?
- 11.11 Hydrogen and oxygen do not normally react at room temperature, but if a trace of platinum black is present, an explosion occurs. Comment.
- 11.12 How does an increase in temperature affect the rate of chemical reaction?
- 11.13 What are meant by the terms
- activation energy
 - transition state
 - life time
 - activated complex
- 11.14 How does a catalyst play a part in decreasing the activation energy of a reaction?
- 11.15 The rate law for a reaction was found to be
 $\text{Rate} = (2.35 \times 10^{-5} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}) [\text{X}]^2 [\text{Y}]$
 What would be the rate of reaction if the concentrations of X and Y were 1 mol/litre ?

ANSWERS TO SELF ASSESSMENT QUESTIONS

- 11.1 (i) b (ii) d (iii) d (iv) c (v) b (vi) b (vii) a (viii) b (ix) c (x) c (xi) b (xii) a (xiii) d (xiv) a (xv) d
- 11.2 (i) b and c (ii) b and d
- 11.3 (i) homogeneous (ii) time interval (iii) zero (iv) first (v) proportionality constant (vi) reactant, product (vii) activation energy (viii) $r = k[\text{H}_2\text{O}_2]$ (ix) $\frac{1}{2} \frac{\Delta[\text{H}]}{\Delta t}$



- 11.4 (i) T (ii) E (iii) T (iv) F (v) F (vi) T (vii) T (viii) F (ix) F (x) T

11.5 Since
$$\frac{-\Delta \text{N}_2}{\Delta t} = -\frac{1}{3} \frac{\Delta [\text{NH}_3]}{\Delta t}$$

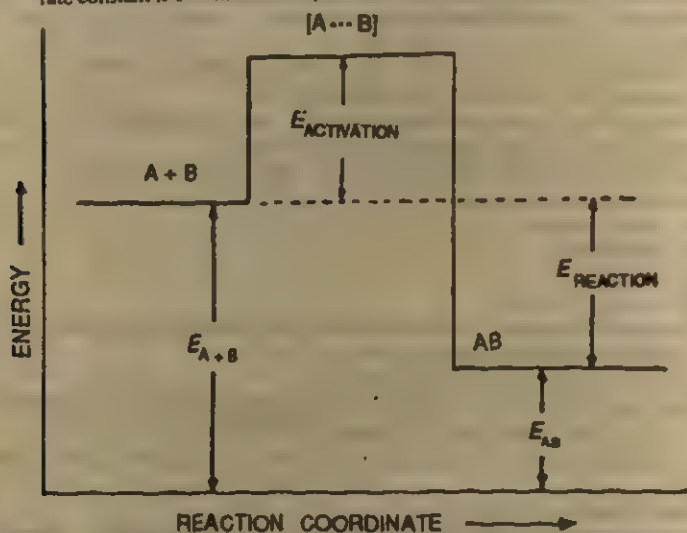
$$\therefore \frac{\Delta [\text{NH}_3]}{\Delta t} = 7.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

11.6 For zero order reaction

$$\text{rate} = \frac{\text{change in concentration}}{\text{time interval}} = k$$

Therefore, units of k will be $\text{mol L}^{-1} \text{s}^{-1}$

11.8 Overall order of reaction is one. For first order reactions $t_{\frac{1}{2}} = \frac{0.693}{K}$ and unit for rate constant is s^{-1} which is independent of concentration



11.9 Concentration in pressure (atm) = (Concentration) (RT)
= Exercise 11.4

Substituting the values

$$6 \times 10^{-2} \text{ mol l}^{-1} \text{ dm}^3 \text{ s}^{-1} = 6 \times 10^{-2} \times 0.082 \times 298 \text{ atm l}^{-1} \text{ s}^{-1} \\ = 1.47 \text{ atm l}^{-1} \text{ s}^{-1}$$

11.10 A catalyst lowers the activation energy of the reactants as well as of the products to the same extent and speeds up both the reactions equally. Here iron, the catalyst will accelerate the decomposition of ammonia.

UNIT 12

Chemistry Of Non-Metals - I

(Hydrogen, Boron, Carbon, Silicon, Nitrogen and Phosphorus)

Who knows not their sense

(These elements).....

Their properties

And power not sees

No mastery he inherits

Over the Spirits

..... J.W. Von Goethe

UNIT PREVIEW

- 12.1 Introduction
- 12.2 Hydrogen
- 12.3 Group 13 elements - general characteristics
- 12.4 Boron
- 12.5 Compounds of boron - borax, boric acid
- 12.6 Group 14 elements - general characteristics
- 12.7 Carbon
- 12.8 Silicon
- 12.9 Silica, silicones and silicates - glass,
- 12.10 Group 15 elements - general characteristics
- 12.11 Nitrogen
- 12.12 Compounds of nitrogen - ammonia, oxides of nitrogen, nitric acid
- 12.13 Phosphorus
- 12.14 Compounds of phosphorus - oxides, oxyacids
- 12.15 Fertilizers

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Differentiate between metals and non-metals with reference to their physical and chemical characteristics.
2. Characterize the non-metals on the basis of their chemical properties, e.g., reaction with acids, etc.
3. Discuss and appreciate the unique position of hydrogen in the periodic table.
4. Understand the concept of allotropy seen among various non-metals.
5. Give reasons for the inert nature of noble gases and extremely reactive behaviour of halogens lying close to them.
6. Cite the principal source of various non-metals and the common methods of their isolation.
7. Explain the atomicity of various non-metals.
8. Compare the variation in properties seen among the elements of the same periodic group.
9. Describe the general degree of reactivity of the elements of each periodic group.
10. Prepare the gases listed in the unit and study their important properties.
11. Understand the nature of bonding in compounds described in this unit and their chemical behaviour.
12. Explain the acceptor behaviour of some of the compounds of boron.
13. Describe the special features of boron, boric acid, silicates, condensed phosphates, etc. and their chemistry.

14. Justify the similarity observed in the reactions of boron and silicon.
15. Justify the statement, "the first element in a group is always different from the other members of the group" by taking the examples of carbon and silicon; nitrogen and phosphorus.
16. Comment on the importance of bonds -Si-O-Si-, P-O-P-, and -P-P- come across while studying the chemistry of silicon and phosphorus.
17. Describe the nature of glass, types of glasses, and some methods of preparation.
18. Describe some of the chemical fertilizers.
19. Give reasons for the inertness of nitrogen.
20. Suggest an experiment to show the solubility of NH_3 .
21. Explain the principle involved in the manufacture of NH_3 gas by Haber's process and nitric acid by Ostwald's process.
22. Describe and demonstrate the reaction of nitric acid on metals and non-metals.
23. Demonstrate the brown-ring test for detecting NO_3^- ion.
24. Comment on the various oxidation states of nitrogen and phosphorus in their compounds.

12.1 INTRODUCTION

Elements, based upon their physical and chemical characteristics and nature of their compounds, are divided into three groups : metals, non-metals and metalloids. You have learnt in Unit 5 about the basis provided by electronic structure for classifying elements into various blocks, groups or families.

With the exception of hydrogen, non-metals are located in the upper right hand region of the periodic table. They have their own characteristic properties and show chemical diversity in their chemical reactions. They include both inert non-metals, e.g., He, Ne, Kr, Xe and extremely reactive non-metals like F, Cl, Br, I. In between these two extremes, we have non-metals of intermediate reactivities, e.g. N, P, O and S. Hydrogen belongs to group 1. It is one of the members of s-block elements.

Most of the elements are metals (80%) and are contained in all periodic groups (except in group 18). Metallic elements are located below and to the left of the step-wise division in the p-block of the periodic table. Some of the elements bordering this line, such as germanium, arsenic and antimony, have similarities to both metals and non-metals and it is difficult to place these, with certainty, in one class or the other. These elements are known as metalloids. The exact location of this line depends upon the particular criterion used, e.g., electrical conductivity, acid-base character of their group oxides, etc.

The general properties that distinguish between metals and non-metals are summarized in Tables 12.1 and 12.2.

The position of metals, non-metals and metalloids is shown below in the periodic table (Fig. 12.1). Hydrogen occupies a unique position in the periodic table.

TABLE 12.1 Physical properties of metals and non-metals

Metals	Non-metals
1. High electrical conductivity	Hardly conduct electricity (graphite, an allotrope of carbon is an excellent conductor of electricity)
2. High thermal conductivity	Good heat insulators
3. High density	Low density
4. Possess lustre	Do not possess any metallic lustre (iodine has shining crystals)
5. Generally solids (mercury is liquid)	Solids (C, S, Se, P, I); Liquids (Br); Gases (O, N, F, Cl)
6. Ductile (can be drawn into wire)	Non-ductile
7. Malleable (can be hammered into sheets)	Brittle in solid state
8. Solid state characterized by metallic bonding	Covalently bonded molecules; inert gases are monoatomic

TABLE 12.2 Chemical properties of metals and non-metals

Metals	Non-metals (except hydrogen and noble gases)
1. Valence shell contains a few electrons; usually three or four	Valence shell contains four or more electrons
2. Electropositive	Highly Electronegative
3. Reducing agents	Oxidizing agents
4. Form cations by losing electrons	Form anions by gaining electrons
5. Form basic oxides which on hydrolysis give hydroxides	Form acidic oxides which on hydrolysis give acids

Most of the non-metals constitute p-block elements. The valence shell electron configuration is $ns^2 np^x$ where x varies from 1 to 6 and n from 2 to 6. There are thirty one p-block elements, six of which are radioactive. In this unit, we shall take up for study the chemistry of hydrogen, boron, carbon, silicon, nitrogen and phosphorus. Although boron belongs to group 13 of the periodic table, many of its chemical characteristics are closer to those of its neighbours, carbon and silicon. Carbon occupies a place in the periodic table just next to boron in the same period and silicon is located diagonally across in the next group. This type of diagonal relationships in chemical properties is also seen in the other elements of second and third periods *e.g.*, between carbon and phosphorus. There is a distinct difference in properties between carbon and silicon; and nitrogen and phosphorus. Silicon and phosphorus belong to the family of 3rd period. The main structural trend for the elements (from Na \longrightarrow Ar) and typical compounds is from ionic solids early in the periods, through covalent and often polymeric solids around group 14 to liquid and gaseous covalent compounds later in the period. In spite the wide range of elements involved, it is very much

H	← NON-METAL																He
Li	Be	B	C	N	O	F	Ne										
Na	Mg	Al	Si	P	S	Cl	Ar										
K	Ca	Ga	Ge	As	Se	Br	Kr										
Rb	Sr	In	Sn	Sb	Te	I	Xe										
Cs	Ba	Tl	Pb	Bi			Rn										
↑ METALS		↑ TRANSITION ELEMENTS		↑ METALS		↑ BRIDGING ELEMENTS BETWEEN ELECTROPOSITIVE AND ELECTRONEGATIVE ELEMENTS (METALLOIDS)		↑ NON-METALS									

PARTIAL SHADING OF Ga Sn As AND Te EXHIBITS SOME PERCENTAGE OF METALLOIDIC BEHAVIOUR

Fig. 12.1 Position of metals, non-metals and metalloids in the periodic table.

possible to make a number of useful generalizations concerning trends in the properties of 2nd and 3rd period elements. The trends in size (covalent radius) follow the normal decrease across the table, and the variation of the first ionization potential (Fig. 12.2) closely follows the variation in atomic size. The trends in reactivity and oxidizing power is in conformity with the change in electronegativity. The large sizes and lower electronegativities of Si, P, S and Cl than the first members of their respective groups (C, N, O and F) lead to a significant differences in the chemistry of these elements. Along with the chemistry of non-metals listed in this unit, we shall also study the manufacture and uses of some important industrial chemicals such as borates, silicates, oxyacids, chemical fertilizers, etc. Some of the observed trends in the properties of p-block elements (non-metals to be discussed also belong to p-block elements) are portrayed in Fig. 12.3.

These non-metals and their compounds play a vital role in chemistry and in our lives. Hydrogen and oxygen react with each other to form H_2O (water), a simple molecule, whose unusual properties are necessary for the development and maintenance of life. Sugar (or carbohydrate), an important source of energy contains C, H, and O. Proteins, the body building materials contain C, H, O and N as their constituents. Detergents, vitamins, fertilizers, medicines, etc., all contain some of the non-metals.

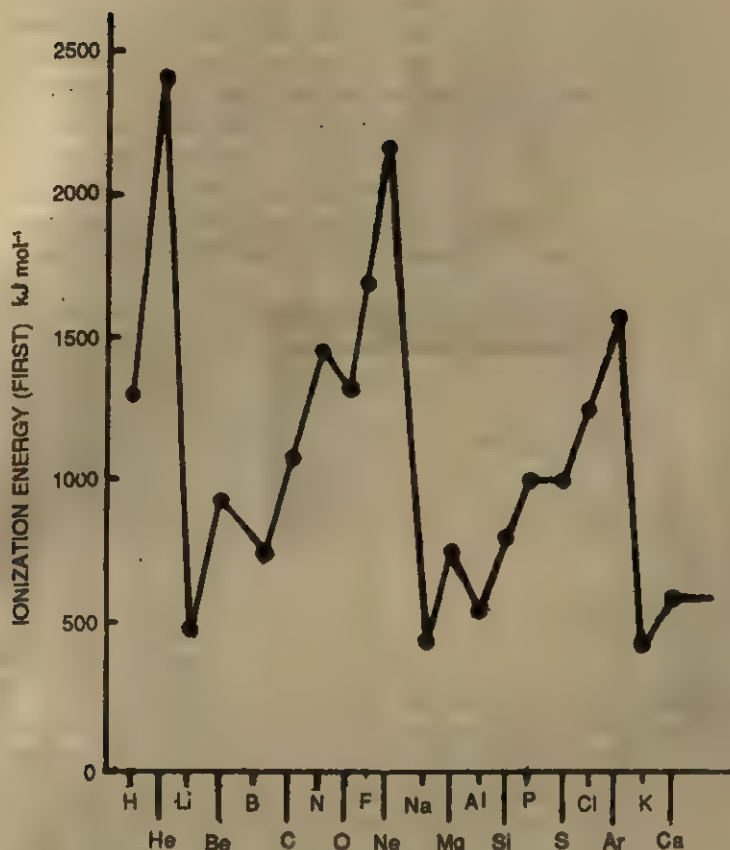


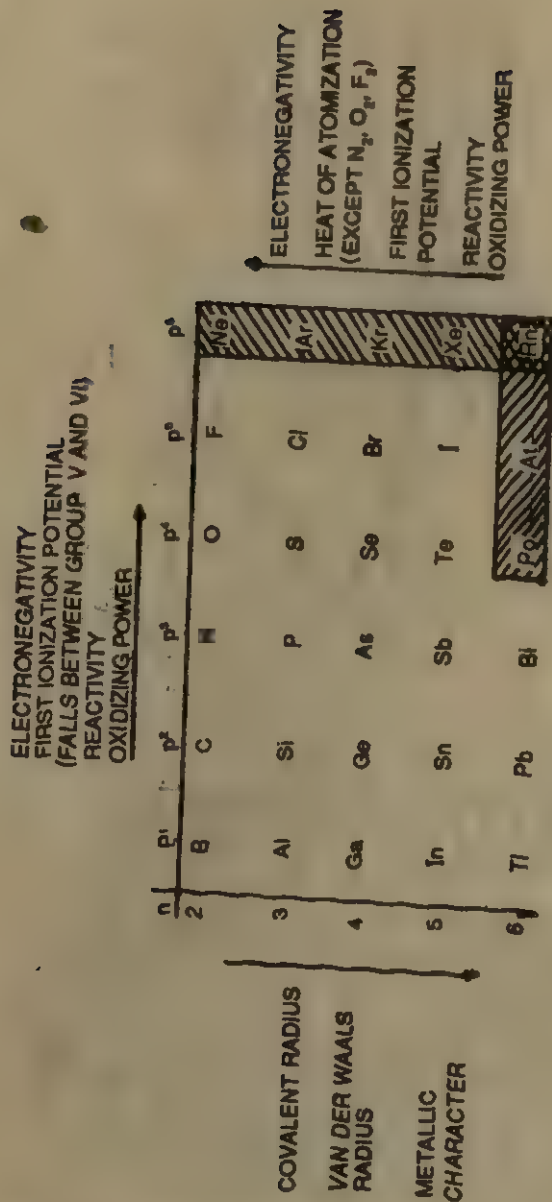
Fig. 12.2 A comparative view of the 1st ionization energies. The 1st ionization energy of hydrogen is very high. It parallels the value seen in the case of halogens.

12.2 HYDROGEN

Hydrogen was discovered in 1776 by Henry Cavendish by the action of dilute sulphuric acid on iron. He investigated its properties and showed that water is the only product when hydrogen burns in air. It was because of this reaction that the 'inflammable air' as called by Cavendish was named hydrogen (Greek, hydrogenon meaning water former) by Lavoisier.

Hydrogen is the first element in the periodic table. It is the lightest element. An atom of hydrogen has one proton and one electron.

Generally, the chemistry of hydrogen can be explained on the basis of its tendency to acquire the electronic configuration of the noble gas, helium either by gaining an electron, e.g., hydride ion, H^- ; or by sharing its electron in H_2 molecule, $\text{H} - \text{H}$; or by accepting and sharing



COVALENT RADIUS
VAN DER WAALS RADIUS
HEAT OF ATOMIZATION (UP TO GROUP IV)
METALIC CHARACTER

INERT GASES (ONLY VAN DER WAALS RADII AND I.P. APPLY)
RADIOACTIVE ELEMENTS

Fig. 12 3. Trends in some properties of the block elements.

a lone-pair of electrons, *e.g.* by a proton from H_2O or NH_3 to form hydronium ion, H_3O^+ , or ammonium ion NH_4^+ respectively.

12.2.1 Position of Hydrogen in the Periodic Table

Hydrogen occupies a unique position in the periodic table.

Hydrogen, being the first element has the simplest atomic structure amongst all the elements. It has a nucleus with single positive charge and one electron in the orbit.

In its properties, it behaves like alkali metals (group 1) as well as like halogens (group 17). Hydrogen, thus, finds its assignment both with alkali metals and halogens. It can lose its only electron to form H^+ ion, and thus, it resembles alkali metals (M) which yield M^+ ions. It can also form H^- ion by gaining one electron similar to halogens (X) forming X^- ions. In its atomicity, it also resembles halogens (both halogens and hydrogen exist in diatomic form).

Hydrogen can also form a single covalent bond with other atoms like C, Si, *etc.* Therefore, hydrogen can be considered as non-metal in respect of some of its properties. Although hydrogen shows similarities in its chemical properties to both alkali metals and halogens, it differs in many ways.

Hydrogen resembles the alkali metals in its ability to form hydrated positive ion, H_3O^+ . But hydrogen does not lose its electron easily as alkali metals do. The ionization energy of hydrogen is very high. (1312 kJ mol^{-1}). In this respect, it resembles halogens (Fig. 12.2) and form numerous covalent compounds. The simplest of these covalent compounds is the diatomic H_2 molecule itself. We call this molecule as dihydrogen to distinguish it from the elemental hydrogen.

12.2.2 Occurrence

Over 90% of all matter in the universe contain hydrogen. Hydrogen because of its reactivity is rarely found in the free state on the earth, though it is present in the Sun and in interstellar space (in isolated form, H(g)). The giant planets Jupiter and Saturn consist mostly of hydrogen. Almost half the mass of the Sun and the stars is accounted for by hydrogen. It is probable that the other elements are built up from hydrogen by nuclear fusion process in the stars. Being light, it tends to collect in the outer atmosphere, or escape from the atmosphere altogether. On the earth hydrogen occurs in the combined form. Only 0.9% by mass of the earth is combined hydrogen and is the 9th element in order of abundance. On the earth most of the hydrogen is present in water, *i.e.*, 11 percent by mass of hydrogen. Hydrogen is present in all acids and bases. It is a constituent of carbohydrates, proteins, fats and oils. Most of the fuels such as wood, coal, coke, cooking gas, petrol, *etc.* also contain hydrogen as a major constituent.

The source of the Sun's energy, which is vital for life on the earth is probably the fusion of hydrogen nuclei to form helium.

12.2.3 Isotopes of Hydrogen

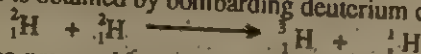
There are two stable naturally occurring isotopes of hydrogen, ^1_1H (proton) and ^2_1H (^2D deuterium). The isotope ^3_1H (or ^3T , tritium) is radioactive and hardly occurs naturally. Their natural abundances are in the ratio $1 : 1.56 \times 10^{-2} : 1 \times 10^{-17}$. Because isotopes of an element have the same electronic structures, their chemical behaviour is alike. But because of their different masses (number of neutrons differ) they show different physical properties.

Hydrogen is usually more reactive than deuterium (heavy hydrogen). Sometimes the rate at which hydrogen and its compounds react differ by a factor of ten. During the electrolysis of water, deuterium ions are discharged more slowly than hydrogen ions. As the electrolysis proceeds, the water becomes richer in deuterium. Pure D_2O , heavy water is eventually obtained as a residue. Electrolytic method is also used on a commercial scale. Heavy water is produced commercially in our country in Baroda (Gujrat), Kota (Rajasthan), Tuticorm (Tamil Nadu) and Thal (Maharashtra). The physical properties of H_2O and D_2O differ from each other (Table 12.3).

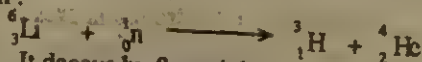
TABLE 12.3 Properties of H_2O , D_2O and T_2O

Properties	H_2O	D_2O	T_2O
Molecular mass	18.015	20.028	22.032
Melting point (K)	273.2	277.01	277.68
Boiling point (K)	373.2	374.62	374.71
Maximum density (g/cm^3)	1.00 (277.18K)	1.1059 (284.43K)	1.2150 (286.6K)
Density at 298K (g/cm^3)	0.997	1.1044	1.2138
Heat of formation, ΔH (kJ mol^{-1})	-285.85	-294.6	-
Heat of vapourization ΔH_{vap} at 373.2K (kJ mol^{-1})	40.66	41.61	-
ΔH_{fus} (kJ mol^{-1})	6.01	6.28	-
ΔH_{ion} (kJ mol^{-1})	56.27	60.33	-
Ionization constant $[\text{H}^+][\text{OH}^-]$ ($\text{mol}^2 \text{L}^{-2}$)	1.008×10^{-14}	1.95×10^{-15}	6×10^{-16}
Dielectric constant	78.39	78.06	-

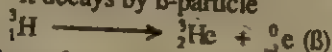
Tritium is obtained by bombarding deuterium compounds with deuterons.



It is also prepared by the irradiation of lithium with slow neutrons in a reaction:



It decays by β -particle

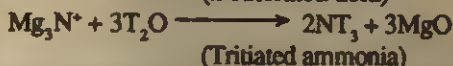
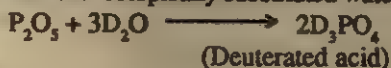


Recently two more isotopes (^4_1H and ^5_1H) of hydrogen have been reported. They are artificial isotopes with short half-lives. They decay

as give below :



Heavy water is used as a coolant and moderator in nuclear reactors. Both deuterium and tritium are most readily produced as oxide (D_2O and T_2O) and most deuterated and tritiated compounds are made directly from the isotopically substituted water, *e.g.*,



Some physical properties for H_2 , D_2 and T_2 are given in Table 12.4.

TABLE 12.4 Comparison of the physical properties of H_2 , D_2 and T_2

Property	H_2	D_2	T_2
Molecular mass	2.016	4.028	6.031
Melting point (K)	13.96	18.73	20.62
Boiling point (K)	20.39	23.67	25.04
ΔH_{vap} (kJ mol ⁻¹)	0.117	0.197	0.250
ΔH_{vap} (kJ mol ⁻¹)	0.904	1.226	1.393
Bond energy (kJ mol ⁻¹) at 298.2K	433.00	443.35	446.9
Internuclear distance (pm)	74	74	74

Apart from the above listed properties their vapour pressures also differ to a large extent. H_2 and D_2 differ in two chemical properties from each other : (i) Dihydrogen is more rapidly absorbed than deuterium and, (ii) with halogens, dihydrogen reacts faster than deuterium due to lower energy of activation for dihydrogen than deuterium.

12.2.4 Atomic and Physical Properties of Hydrogen

Despite its very simple electronic structure ($1s^1$) hydrogen exists in over forty forms. Most of these states have been well characterized. They include in the first instance, atomic, molecular, and ionized species in the gas phase, H , H_2 , H^+ , H^- , H_2^+ , H_2^- ; in the second instance, from the existence of three isotopes ${}^1_1\text{H}$, ${}^2_1\text{H}$ (D) and ${}^3_1\text{H}$ (T) and corresponding of D , D_2 , HD , DT , *etc*; and finally from the existence of nuclear spin isomers of H_2 , D_2 , *etc*.

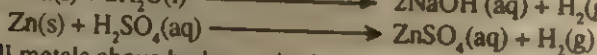
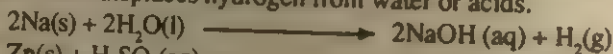
Dihydrogen molecule is a very stable, colourless, odourless gas with a very low m.p. and b.p. It dissociates into hydrogen atoms to an appreciable extent only above $> 2000\text{K}$; the percentage of atomic hydrogen is 0.081 at this temperature, and this rises to 7.85% at 3000K and 95.5% at 5000K. However, atomic hydrogen is prepared easily in low-pressure glow discharges. Atomic and molecular properties of hydrogen are given in Table 12.5.

TABLE 12.5 Atomic and molecular properties of hydrogen

Atomic properties		Molecular properties	
Atomic radius (pm)	37	Melting point (K)	13.96
Ionic radius H^+ (pm)	210	Boiling point (K)	20.39
Electron affinity (kJ mol ⁻¹)	73	Density (g/cm ³)	0.0899
Ionization energy (kJ mol ⁻¹)	1312	Internuclear distance (pm)	74
Electronegativity	2.1	Bond energy (kJ mol ⁻¹)	433.00

12.2.5 Preparation of Dihydrogen

1. Action of water or dilute mineral acids on metals produce dihydrogen. Metal displaces hydrogen from water or acids.



All metals above hydrogen in the electrochemical series (Unit 10) displace dihydrogen from acids. Dihydrogen is prepared in the laboratory by the action of dilute H_2SO_4 or HCl on granulated zinc. The gas is collected by the downward displacement of water. The apparatus employed is portrayed in Fig 12.4

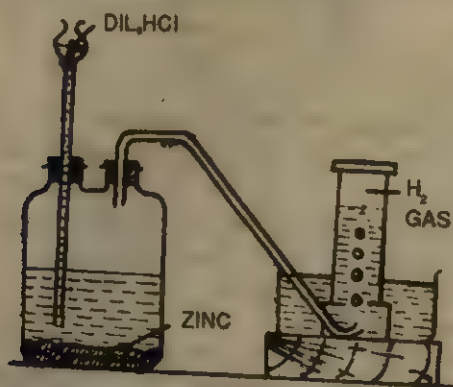


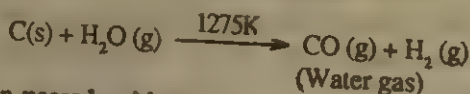
Fig. 12.4 Laboratory preparation of dihydrogen.

To remove any trace of acid the gas is bubbled through KOH solution. Dihydrogen can be dried by passing through concentrated sulphuric acid or phosphorus pentoxide.

2. Pure dihydrogen is produced by the electrolysis of acidified water. This method is, however,

quite expensive. It is also a byproduct of commercial preparation of chlorine and sodium hydroxide by electrolysis of brine (sodium chloride solution).

3. Dihydrogen is also manufactured from water gas (Bosch's process), steam is passed through hot coke, the mixture of gaseous products is known as water gas.

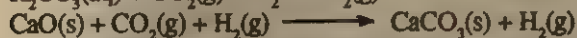
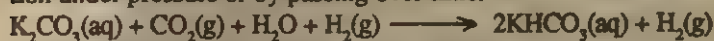


Water gas is then passed, with excess steam, over a heated iron (III) oxide or cobalt oxide catalyst at 673K. The carbon monoxide then reacts

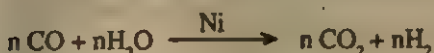
with the steam to form more or anyarogen.



Carbon dioxide is removed by bubbling gases through hot K_2CO_3 solution under pressure or by passing over lime.



This method is now not much in use. Now coke has been replaced by methane or naphtha (alkanes containing four to ten atoms of carbon). A mixture of steam and hydrocarbons is passed over a nickel catalyst.



Carbon dioxide can be removed by either of the above methods.

Hydrocarbons are cracked at high temperature and during cracking we get dihydrogen as a by-product. Methods of preparation and manufacture for dihydrogen gas are summarized in Fig. 12.5.

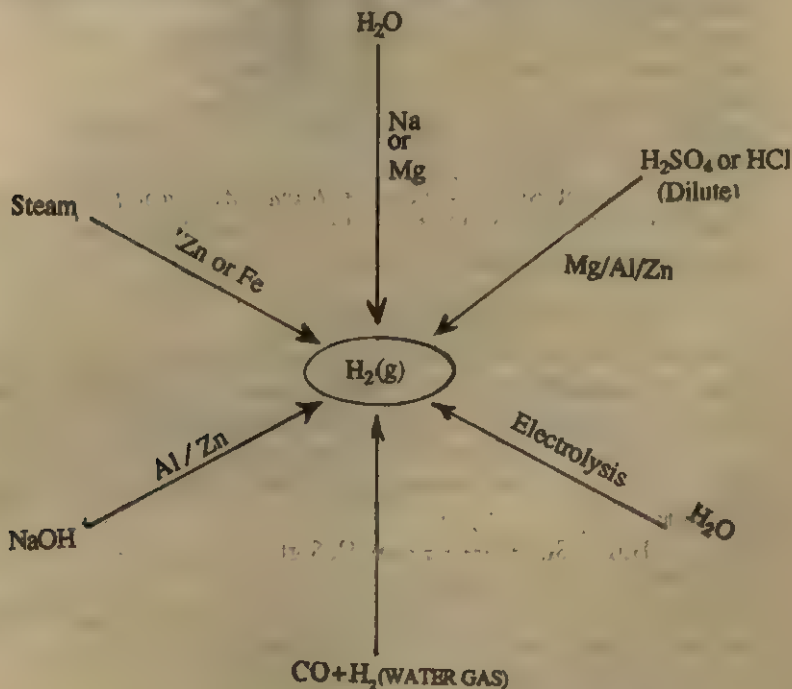


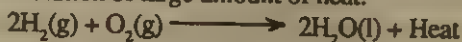
Fig. 12.5 Methods of preparation and manufacture of dihydrogen gas

12.2.6 Properties and Reactions of Dihydrogen

Dihydrogen is a colourless, odourless and tasteless gas which is almost insoluble in water and is liquefied only with great difficulty. It is the lightest known gas.

Dihydrogen does not show any reaction with litmus, and hence, it is neither acidic nor basic.

Dihydrogen burns in air (or oxygen) with a blue flame (highly inflammable) producing water (Fig. 12.6). The reaction is accompanied with the evolution of large amount of heat.



Dihydrogen does not support burning.

1. Reaction with non-metals

Dihydrogen reacts with almost all the elements (except noble gases) under different conditions. Because of its high bond dissociation energy (433 kJ mol^{-1}) dihydrogen is not very reactive. At high temperatures or in the presence of catalysts, it reacts with many non-metals

forming covalent hydrides. It combines with chlorine in the bright sunlight or when its burning flame comes in the contact of chlorine

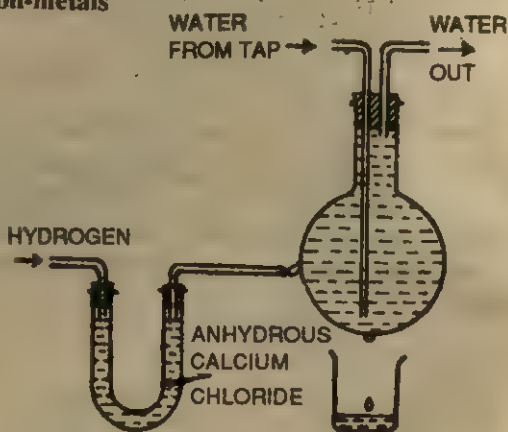
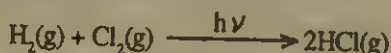
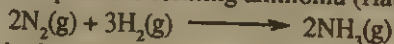


Fig. 12.6 Burning of dihydrogen in air forming water



Bromine and iodine combine only on heating. It also combines with dinitrogen in the presence of a catalyst under suitable conditions of temperature and pressure forming ammonia (Haber's process).

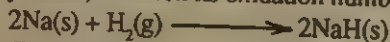


Dihydrogen, on passing through boiling sulphur, forms hydrogen sulphide.



2. Reaction with metals

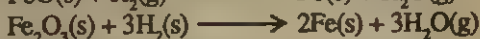
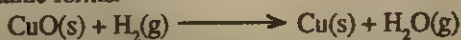
Dihydrogen reacts with alkali and alkaline earth metals to form saltlike hydrides, in which its oxidation number is -1.



Direct union of the transition metals, *e.g.*, Pd, Ni, Pt, *etc.* (d-block elements) with dihydrogen gas leads to formation of **interstitial hydrides** in which hydrogen atoms, because of their small size, occupy interstitial holes (UNIT 3) in the metallic crystals.

3. Reaction with compounds

Dihydrogen acts as a reducing agent. It reduces metal oxides (oxides of metals present below hydrogen in the electrochemical series) to their metallic forms.



As few typical reactions of dihydrogen are portrayed in Fig. 12.7.

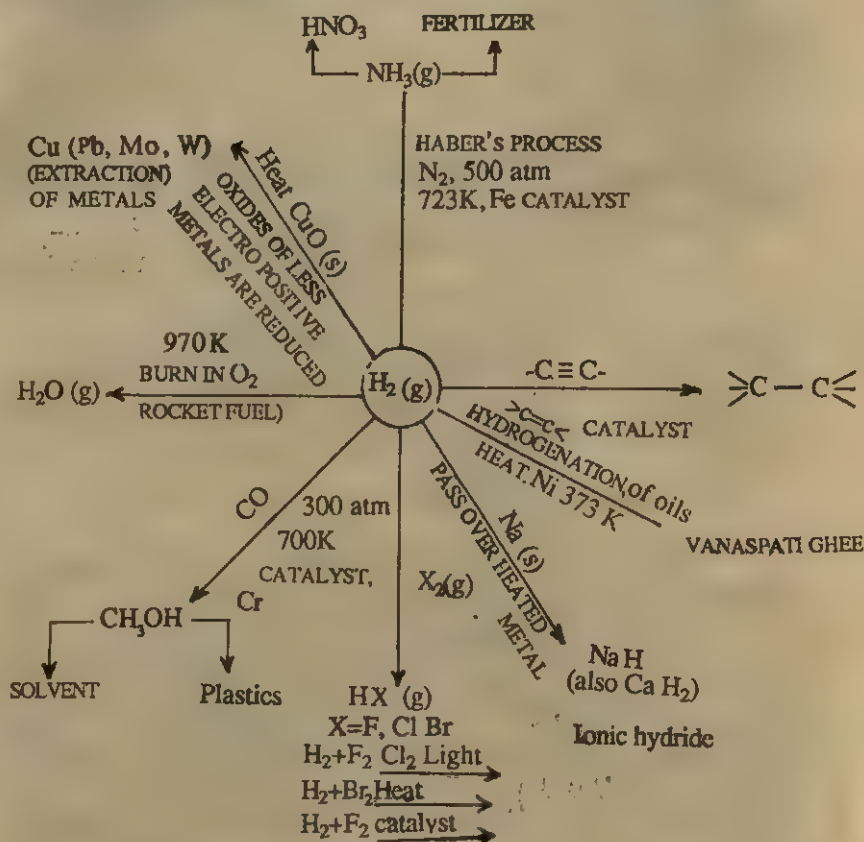


Fig. 12.7 Some typical reactions of dihydrogen.

12.2.7 Uses of Dihydrogen

1. Dihydrogen was used earlier in filling balloons and airships. However, on account of its highly inflammable nature, it has now been re-

placed by helium. It is still used in meteorological and cosmic research balloons because of its extremely low density.

2. It is used in the manufacture of ammonia (by Haber's process) which is the basis of many fertilizers. Fertilizers are used extensively to yield better crops.

The major bulk of commercially produced dihydrogen is used in producing hydrochloric acid, explosives, plastics and a large number of organic chemicals. (Fig. 12:8)

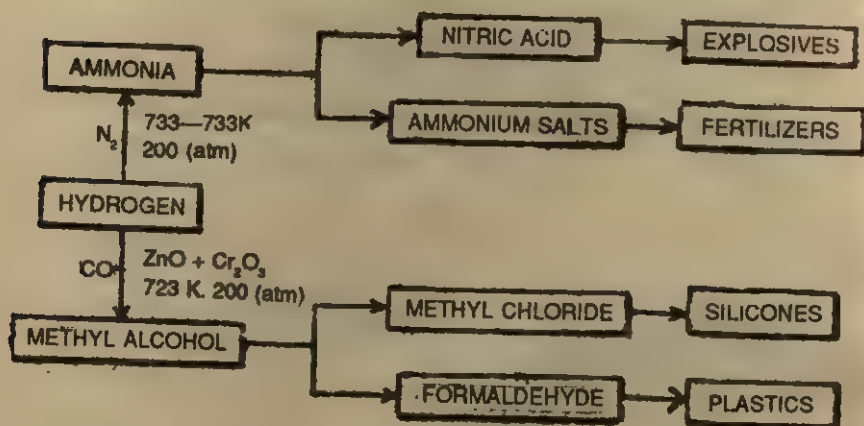
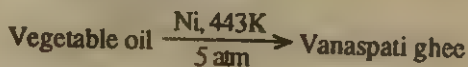


Fig. 12. 8 Flow chart illustrating the uses of dihydrogen

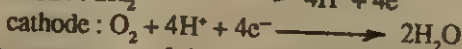
3. It is used in the manufacture of vanaspati ghee. This process is called hydrogenation or hardening of oils. The hydrogenated products have superior keeping qualities.



4. Dihydrogen is used in the manufacture of petrol. This is done by hydrogenation of powdered coal or coke at a moderately high temperature and under very high pressure.

5. The high heat of combustion of hydrogen makes it valuable as a fuel. It is used as a fuel mixed with other gases in coal gas and water gas.

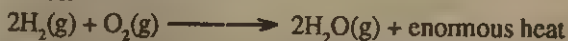
Liquid dihydrogen has been used as a rocket fuel in fuel cells by generating electrical energy; such fuel cells have been used in manned space-crafts (Gemini, Saturn and Apollo) by reaction of dihydrogen and dioxygen without generating any heat. The electrode reactions are :



For proper use of the reaction to proceed at a useful rate a catalyst is used. In addition to electrical power, the fuel cell also produces

pure drinking water for astronauts. Liquid hydrogen is likely to be developed as fuel for motor vehicles in future.

6. Oxy-hydrogen flames which have a temperature of about 2273K are used for welding and cutting metals. The flames are also used for fusing alumina to produce rubies and sapphires used as bearings (jewels) in watches.



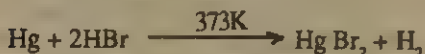
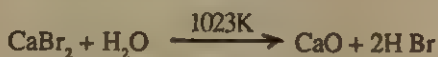
7. It is used as a reducing agent in certain metallurgical operations to reduce oxides to metals (e.g., Mo, W) and to produce a reducing atmosphere. Its use in direct reduction of iron ores in steel manufacturing is being tried.

HYDROGEN - A FUTURE FUEL

Apollo 11 attached to its rocket (Saturn V), that made the landing of Neil Armstrong possible on the moon and used in the - USA space programme were powered by liquid dihydrogen.

Dihydrogen gas has been proved to be a potential fuel for use in internal combustion engines and fuel cells.

However, the lack of availability of free dihydrogen limits its use. Being of highly inflammable nature, it is difficult to store and distribute safely. The technology already exists for producing dihydrogen electrically from water but a lot of energy has to be used. Non-electrolytic sources of dihydrogen have also been investigated. The problem which the scientists world over are facing is how to transfer the correct amount of free energy to a water molecule in order to decompose it. In the last few years thousands of such thermochemical water splitting cycles have been identified. One potentially useful sequence is



The stage is thus set, and further work to establish safe and economically viable sources of dihydrogen for domestic and other general energy use seems destined to grow as a potential field of research for some while.

12.3 GROUP 13 ELEMENTS GENERAL CHARACTERISTICS

Group 13 of the periodic table contains boron, aluminium, gallium, indium and thallium. In keeping with the periodic trend, the group 13 elements are less metallic than those of the first s-block elements. Within the group, there is a great variation in basicity. Boron the smallest atom

in this group, is non-metallic. The other elements in the group are metals and have a greater tendency to form ionic rather than covalent compounds. This is the first group in which change from non-metallic towards the metallic condition occurs.

As seen with s-block elements, boron behaves differently from the other members of the group. This difference in properties has been attributed to the difference in size and electronegativity of first and second members of the groups being much larger than that between any other successive group elements. Their valence shell electron structure is $ns^2 np^1$ and generally form compounds with +3 oxidation state. Boron form compounds with -3 and +3 oxidation states. The electronic configuration has a strong influence on the properties of these elements. Some properties of boron and aluminium are listed in Table 12.6.

TABLE 12.6 Some properties of boron and aluminium

Property	B	Al
Covalent radius (pm)	82	125
Ionic radius, M^{3+} , (pm)	20	50
Ionization potential (kJ mol^{-1})	Ist	800
	IInd	2427
	IIIRD	3658
Electronegativity	2.0	1.45
Electron affinity (kJ mol^{-1})	15	26
Oxidation state	-3, +3	+3
Physical state	solid	solid
Density at 298K (g/cm^3)	2.34	2.70
Melting point (K)	2573	933
Boiling point (K)	2823	2600

12.4 BORON

Boron is the first member of group 13 of the periodic table and is the only non-metal of this group, though still showing slight indications of a metallic influence. It has three valence electrons in the valence shell. Boron has a fairly high electronegativity value and shows largely non-metallic characteristics.

Because of its low electronegativity and high ionization potential it does not form simple negative ions. Boron forms a variety of covalent molecular compounds, a property common to carbon and silicon. In many respects, the chemistry of boron is similar to that of silicon (Table 12.7). This type of similarity is termed diagonal relationship. Boron, in its compounds, has less number of electrons than the maximum possible number, i.e., a total of four electron pairs (2s, 2p). Such compounds are called **electron deficient compounds**. It tends to achieve electronic saturation, i.e., fully occupied outer electron shells in a variety of ways, viz,

- (i) Multiple bonding, *e.g.*, BF_3 , in which a lone pair of electrons on each fluorine atom may be used in a $\text{B} \leftarrow \text{F}$ dative bond involving the vacant p orbital on the boron atom.
- (ii) Formation of complexes in which electrons are received from a donor molecule, *e.g.*, $\text{F}_3\text{B} \leftarrow \text{NH}_3$. Boron compounds, thus behave as Lewis acids.

Boron is not a common element but it is widely distributed in nature. The most widely known compound of boron is borax, the name being derived from an Arabic word given to fluxes in general. Boron was first isolated in 1808 by Gay-Lussac and Thenard by the reduction of B_2O_3 with potassium.

12.4.1 Occurrence and Isolation

Boron is relatively a rare element constituting about 0.001% of the earth's crust. It owes its rarity to the ease with which it undergoes transmutation. Boron does not occur free in nature. The principal ores are borates, *e.g.*, borax or tinacal ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and kernite or rasorite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$). Other less important sources are the form of complex borates, *e.g.*, colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$), ulexite or boronatrocalcite ($\text{CaB}_4\text{O}_7 \cdot \text{NaBO}_2 \cdot 8\text{H}_2\text{O}$) and boracite ($2\text{Mg}_3\text{B}_4\text{O}_{13} \cdot \text{MgCl}_2$).

Commercial viable deposits of borates are found in California (U.S.A.), USSR, South America and Turkey. In India boron is found in Pugga valley (Eastern Kashmir) Ladakh and Sambhar Lake (Rajasthan). The most important and abundant boron mineral is 'tourmaline', a complex aluminosilicate containing about 10% of boron.

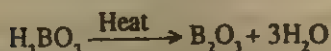
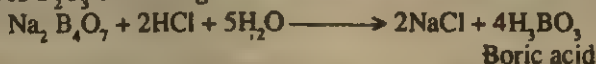
The metallurgical operation of boron from minerals involves two steps :

1. The preparation of boron trioxide, and
2. The reduction of the oxide to elemental boron

It is quite difficult to prepare pure boron because of its high m.p., the corrosive nature of the liquid and the ease with which it combines with the reducing agent employed.

Boron may be obtained in two forms, **amorphous and crystalline**. An impure amorphous boron can be obtained as follows :

Sparingly soluble boric acid, produced on treating borax with HCl , gives B_2O_3 on heating.



Boron trioxide, in turn, on heating with magnesium powder is reduced to boron metal.



After cooling, the product is washed successively with strong base, HCl and HF to remove unreacted substances and the product MgO. Finally the product is washed with hot water and dried in steam oven, when the amorphous form is obtained as a brown powder. The product so obtained contains microcrystalline boron (95.98% pure) and metal borides.

Crystalline form of boron can be obtained by the following methods :

- (1) By pyrolysis of BI_3 on tantalum, tungsten or boron nitride surfaces at 1073-1273K.
- (2) By reduction of volatile BCl_3 and BBr_3 with H_2 at 1273K on a tantalum or tungsten filament.
- (3) $2\text{BBr}_3 + 3\text{H}_2 \longrightarrow 2\text{B} + 6\text{HBr}$
- (4) By thermal decomposition of boron hydrides.
- (5) By the electrolytic reduction of fused mass of borates or other boron compounds (e.g., KBF_4) at 1000K or above.

12.4.2 Properties and Chemical Reactions of Boron

Natural boron consists of two isotopes, $^{10}_5\text{B}$ (19.6%) and $^{11}_5\text{B}$ (80.4%). A variety of forms of elemental boron exists. X-ray diffraction methods have revealed the structures of one tetragonal and two rhombohedral forms. All these forms are based on icosahedral B_{12} units (Fig. 12.9), linked together in several different ways.

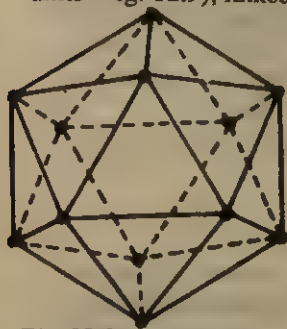


Fig. 12.9 Icosahedral arrangement of boron atoms

Crystalline boron is extremely inert chemically. It has metallic luster. It behaves like a semiconductor. It is very hard being only second to diamond in hardness with a melting point 2573K (Table 12.6). The chemical reactivity of boron depends greatly upon whether the impure amorphous or the crystalline form is involved.

Boiling HCl or HF has no effect on pure boron, and it is only slowly

oxidized by hot concentrated HNO_3 , HClO_4 or H_2SO_4 yielding boric acid. Boron reacts vigorously with fused alkalis, Na_2O_2 or $\text{Na}_2\text{CO}_3 + \text{KNO}_3$ (fusion mixture) at high temperatures to give borates and hydrogen.

Amorphous boron is a reactive substance which burns readily when heated in air, forming oxide and nitride. Further this form of boron is also oxidized by H_2SO_4 or HNO_3 forming boric acid. Amorphous boron dissolves slowly in hot concentrated aqueous alkalis while crystalline form remains unattacked.

Boron reacts with many metals to give hard and inert binary compounds called metallic borides. Usually they are interstitial compounds. Some of the typical reactions of boron and methods of its isolation are illustrated through Fig. 12.10.

12.4.3 Uses of Boron

Because of the very high ability of boron-10 isotope to absorb neutrons, metal borides are used in nuclear industry as protective shields and control rods. Boron filaments are used in electric bulbs. It is also used in some metallurgical processes as a deoxidizer. The boron filament is one of the constituents of the composite material for aircraft and space shuttles. Traces of the metal are used in hardening steels. It also finds use in making transistors.

12.5 COMPOUNDS OF BORON

12.5.1 Hydrides of Boron

Boron forms a series of the volatile hydrides which resemble, in some respects, the hydrides of carbon and silicon. In view of its trivalency, it is expected to form a simple hydride BH_3 . However, the

simplest known and stable hydride is diborane, B_2H_6 (BH_3 is very unstable). Boron does not react directly with hydrogen. The boron hydrides are sometimes called boranes by analogy with the alkanes (hydrocarbons).

Diborane is made by treating sodium borohydride, NaBH_4 , with concentrated

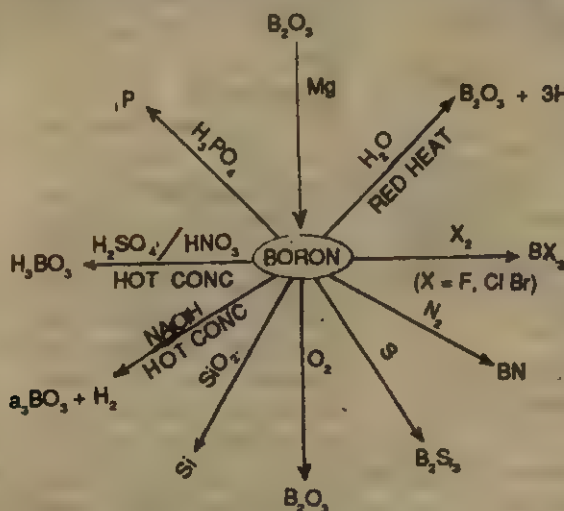
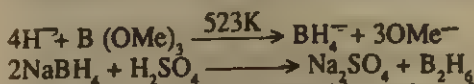
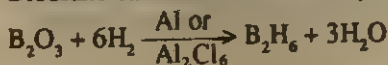


Fig. 12.10 Some reactions of elemental boron and a method for its isolation

H_2SO_4 and other non-aqueous acids (H_3PO_4). Generally NaBH_4 is obtained from trimethyl borate and sodium hydride, i.e.,



Biborane can also be obtained by action of hydrogen on boric oxide.



Pyrolysis of diborane is the source of other higher hydrides. Diborane is a colourless gas.

Since boron has one electron less than carbon, diborane cannot be structurally identical with ethane, C_2H_6 , because it is electron deficient. The electron deficiency is overcome by the formation of three centre bonds.

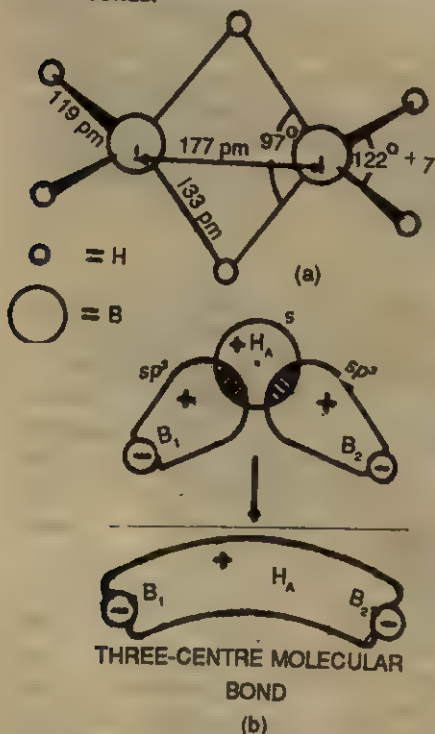


Fig. 12.11 (a) Bridge structure of diborane. (b) Three centred bonds in diborane.

boron atom and one from each hydrogen atom. An sp^3 hybrid orbital from each boron atom overlaps the 1s orbital of the hydrogen atom giving a delocalized orbital containing one pair of electrons but covering all the three nuclei. This makes one of the bridges. This is known as three-centre electron pair bond, B-H-B. The molecule of diborane contains two such bonds. Due to repulsion between the two hydrogen nuclei, the delocalized orbitals or bridges are bent away from each other in the middle. This is why the hydrogen bridge. Orbital is shifted upwards in the middle. The other bridge orbital will be shifted downwards.

Some important reactions (also based on its electron deficient nature) are given in Fig. 12.12.

Diborane has been found to possess a bridge structure (Fig. 12.11) in which each B atom is bonded to two H atoms (called terminal H atoms) by regular electron-pair bonds. The resulting BH_2 fragments are bridged by two H atoms (evidenced by electron diffraction and Raman and infrared spectroscopy). The bridge H atoms are in a plane perpendicular, i.e., one above and one below the plane to the rest of the molecule and prevent rotation between the two boron atoms.

The nature of bonds in hydrogen bridges is now well established. The two hydrogen bridges involve a total of four electrons, one electron from each hybrid boron atom and one from each hydrogen atom.

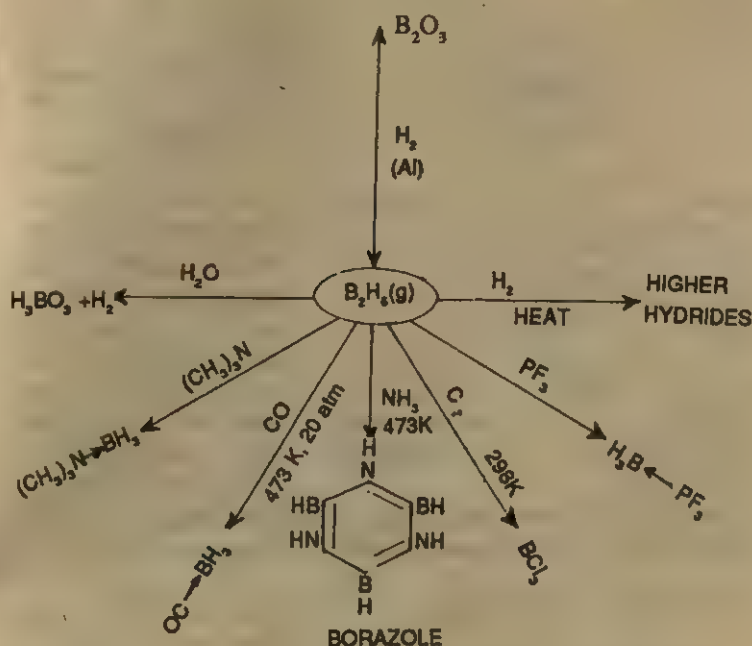
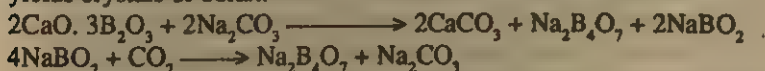


Fig. 12.12 Some reactions of diborane.

12.5.2 Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$

Borax is the most important compound amongst borates. It occurs naturally as such in certain dried up lakes of India (Kashmir Valley) Tibet and California (U.S.A.).

Borax can also be obtained from certain minerals such as boracite, colemanite, boron atocalcite, etc. The mineral colemanite is finely powdered and boiled with sodium carbonate solution. The insoluble calcium carbonate is filtered off; the filtrate on concentration yields crystals of borax.



Its structure is based on planar BO_3 units and tetrahedral BO_4 units. For borax, although the formula is often written as $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, a better formulation for borax is $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ (Fig 12.13).

Aqueous solution of borax is alkaline. On hydrolytic decomposition, it produces sodium hydroxide and boric acid.

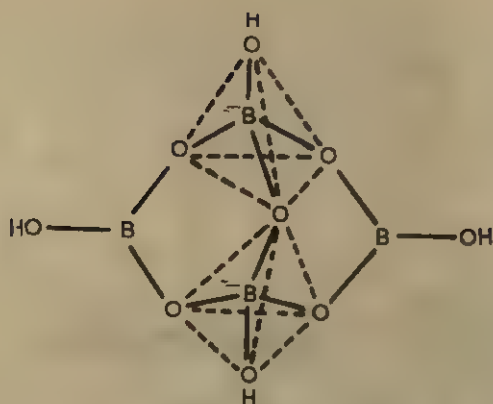
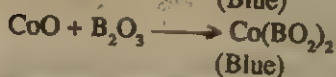
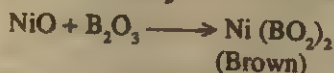
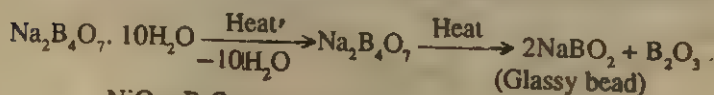


Fig. 12.13. Structure of the anion $B_4O_5(OH)_4^{2-}$ or $H_4B_4O_9^{2-}$, two boron atoms have trigonal planar, and two tetrahedral stereochemistry.

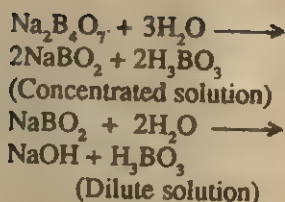
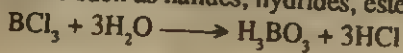
and which assumes characteristic colours. This forms the basis of 'borax bead test' for the qualitative analysis of various cations.



Uses: Large quantities of borax are used in the manufacture of optical and hard glasses, enamels and glazes for pottery. It is an important ingredient of a variety of detergents, soaps, water-softening compounds (use in water softening and washing compounds depends upon the alkaline character of its solutions and the insolubility of the borates of calcium and magnesium) adhesives, cosmetics and glazed paper. It is also used as an antiseptic in making medicinal soaps, in the preservation of food, as a flux in soldering, in stiffening candle wicks, as well as in the manufacture of leather, paper and plastics.

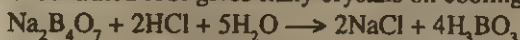
12.5.3 Boric Acid $B(OH)_3$

Orthoboric acid, usually called 'boric acid' (trivial name) is obtained on hydrating B_2O_3 . It is prepared by the hydrolysis of various compounds such as halides, hydrides, esters, etc.

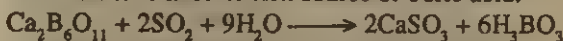


It swells into a white mass on heating and loses water. On further heating it melts to form a transparent glassy solid called 'borax bead'. The borax bead further can dissolve many metal oxides to form metaborates

Boric acid can also be processed from natural sources. Soffioni (steam jets of the volcanic vapour in Tuscany) on condensation and concentration yields boric acid. Aqueous solution of borax on treating with concentrated HCl gives flaky crystals on cooling.

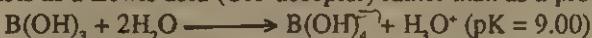


Colemanite is another rich source of boric acid.

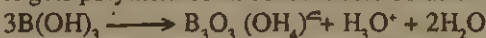


Boric acid crystallizes out on cooling and calcium bisulphite remains into solution.

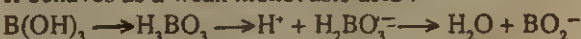
Boric acid is a white crystalline solid. In dilute solutions, boric acid acts as a Lewis acid (OH^- -acceptor) rather than as a proton donor:



It gets polymerized in concentrated solution :



It behaves as a weak monobasic acid :

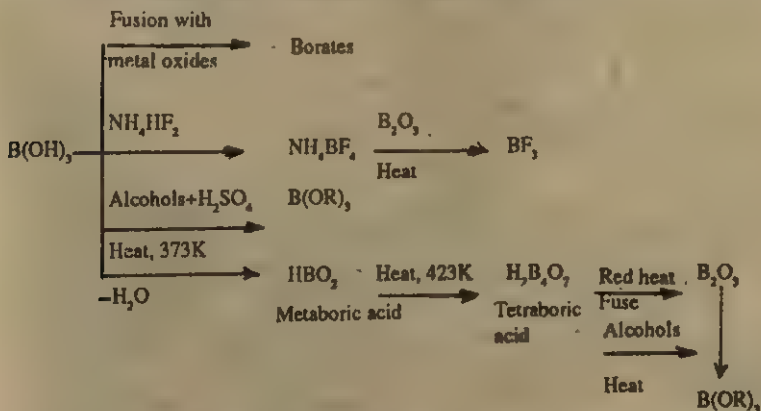


Thus, on titration with NaOH,



The end point is not sharp due to hydrolysis of NaBO_2 . On complexing the BO_2^- ion with polyhydroxy compound with cis-OH groups such as glycerol, mannitol or sugars, the acid strength is increased.

Some reactions of boric acid are shown below :



In the boric acid, each B atom is bonded to three oxygen atoms, arranged at the corners of an equilateral triangle. This can be predicted from hybridization of the available orbitals.

Thus, it assumes a layer structure of planar $\text{B}(\text{OH})_3$ units linked together by hydrogen bonding as shown in Fig. 12.14.

Uses : Aqueous solution of boric acid is commonly used as a mild antiseptic. Boric acid also finds use in the manufacture of heat

and chemical resistant borosilicate glass (e.g., pyrex) and certain optical glasses.

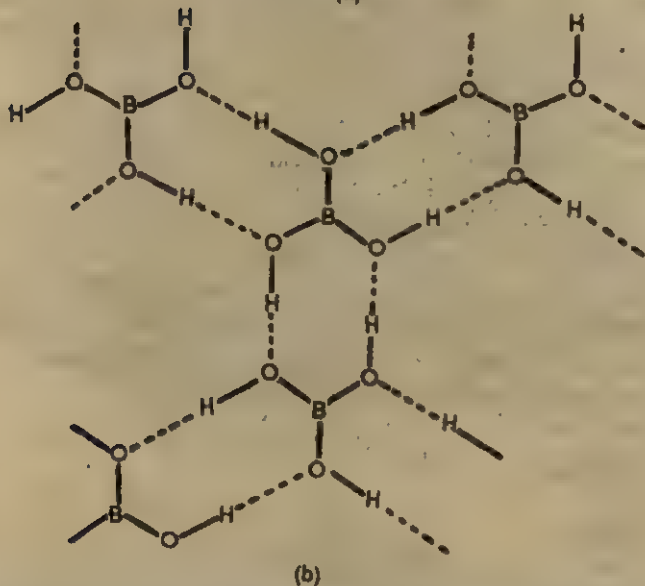
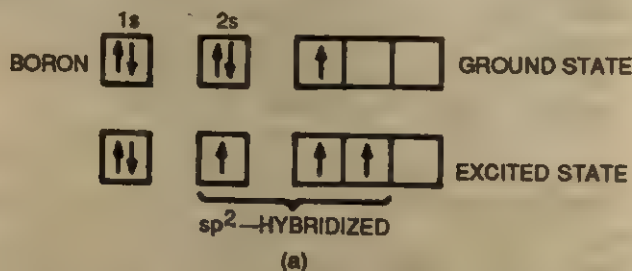


Fig. 12.14 (a) Hybridization scheme of B atom. (b) Layer structure of orthoboric acid, hydrogen bonds are represented by dotted lines.

12.6 GROUP 14 ELEMENTS - GENERAL CHARACTERISTICS

Group 14 of the periodic table contains carbon, silicon, germanium, tin and lead. The elements range from non-metallic carbon, through semi-metallic silicon and germanium to the weakly electropositive metals tin and lead. The properties of the elements (Unit 15) show the expected trends for a related family of elements in the periodic table. Their valence shell electron structure is $ns^2 np^2$. Each exhibits a maximum oxidation state +4; these elements, especially heavier ones also show an oxidation state +2. The values of electronegativity and ionization potential indicate that there must be a considerable degree of covalency in the chemical bonding of these elements. Carbon behaves differently from the other members of the group.

12.7 CARBON

Carbon, the most important element of group 14, plays a vital role in our existence. Its compounds are the stuff of life, the nutrients, the building blocks of plants and animal tissue, and regulate biochemical reactions. Petroleum and petrochemicals, also the carbon compounds, are the primary fuels for our industries and the raw materials for plastics and synthetic fibers.

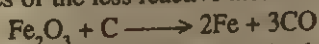
Elemental carbon occurs as graphite and diamond, and large deposits of carbon compounds occur as coal, petroleum natural gas and mineral carbonates.

Many aspects of carbon have already been discussed in Unit 7. Some important properties of carbon and silicon along with that of boron are listed in Table 12.7

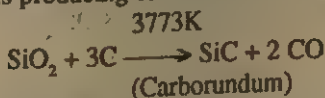
TABLE 12.7 Properties of boron, carbon and silicon

Property	Boron	Carbon	Silicon
Electronic structure	[He], 2s ² , 2p ¹	[He]2s ² , 2p ²	[Ne], 3s ² , 3p ²
Covalent radius (pm)	82	77	117
Ionization potential (kJ mol ⁻¹)	Ist	1086	786
	IInd	2354	1573
	IIIRD	4622	3232
	IVth	6223	4351
Heat of vapourization			
ΔH _{vap} (kJ mol ⁻¹)	504.5	—	383
Electronegativity	2.0	2.5	1.74
Electron affinity (kJ mol ⁻¹)	15	123	135
Oxidation state	-3, +3	+4	+4
Metal/non-metal properties	Non-metal	Non-metal	Semi-metal
Density (g/cm ³) (298K)	2.34	3.514	2.336
Melting point (K)	2573	4273	1693
Boiling point (K)	2823	—	3553

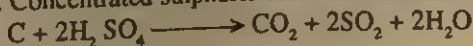
Although carbon is unreactive at room temperature, it reacts with a number of substances on heating. On combining with dioxygen it forms both carbon monoxide and carbon dioxide. It reduces the oxides of the less reactive metals forming metal and carbon monoxide.



This reaction takes place in the blast furnace reduction of iron ore with coke. With oxides of more electropositive metals, carbon forms corresponding metal carbides. It also reacts with oxides of certain non-metals producing carbides.



Steam is reduced by carbon at high temperature. Water gas is produced from which dihydrogen gas is produced on a commercial scale. Concentrated sulphuric acid oxidizes carbon to carbon dioxide.



12.8 SILICON

Silicon is a member of group 14 but there are notable differences from carbon, on the one hand, and the heavier metals (Ge, Sn and Pb) of the group on the other. Silicon ranges from such bulk commodities as concrete, clays, and ceramics, through more chemically modified systems such as soluble silicates, glasses and glazes to the modern industries based on silicone polymers and solid state electronic devices. The name of the element, silicon was proposed by Thomas Thomson in 1831, the ending 'on' being intended to show its similarities with carbon and boron (Table 12.7). Its compounds silica and silicates have been intimately associated with the evolution of mankind.

Its outermost shell is four electrons short of the next inert gas configuration. It shows a covalency of four. In silicates, it shows - 4 oxidation state. Silicon assumes a maximum coordination number of six (because of the use of 3d orbital in its compounds and most characteristic number is four. Some physical properties of silicon are compared with that of boron and carbon in Table 12.7.

Silicon is notably more volatile than carbon (Table 12.7) and has very low energy of vapourization, thus reflecting the smaller Si-Si bond energy amongst the elements of group 14.

Bond energy data (Table 12.8) show that C - C bond is stronger than the bond between Si-Si. Carbon has a strong tendency to link together to form chains and rings. This property of self linkage (catenation) is of an exceptional degree in carbon but exists to a relatively small degree in silicon also. Hydrides with chains of 10 silicon atoms have been made. Silicon forms much stronger bonds with oxygen, fluorine and chlorine than with itself or hydrogen (Table 12.8). In contrast to the hydrocarbons, the silicon compounds with Si-Si or Si-H bonds are generally reactive, *e.g.*, hydrides of silicon, silanes.

Silicon has the diamond structure (Unit 6) but the Si-Si bonds are longer and weaker than the C-C bonds, and so the melting point and boiling point of silicon are lower than that of carbon (Table 12.7). Silicon has no allotropic form similar to graphite. This means silicon has a much smaller tendency to form multiple bonds than carbon. Both carbon and silicon form dioxides but they differ in various respects. Carbon dioxide is gas whereas silicon dioxide is a high melting solid.

- (i) Si-O is stronger than C-O,
- (ii) Much smaller tendency to form multiple bonds than carbon, and
- (iii) Availability of 3d orbitals for bonding.

TABLE 12.8 Bond energies involving carbon and silicon

Bond	Energy(kJ)	Bond	Energy (kJ)
C—C	347	Si—Si	226
C—H	414	Si—Si	318
C—O	360	Si—O	464
C—F	389	Si—F	598

12.8.1 Occurrence and Isolation of Silicon

Silicon is second to oxygen in abundance (27.72% by mass) in the earth's crust. It occurs as silica, SiO_2 (in the form of quartz, flint, opal, sand, agate, mica, etc.) and as silicates. Impure forms of silica include sand and sandstone. Important silicates are : felspar, KAlSi_3O_8 (found in igneous rocks); clay or kaolin, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$; and asbestos, $\text{Ca}_2\text{Mg}_3\text{Si}_2\text{O}_9$.

The great affinity of silicon for oxygen delayed its isolation as the free element until 1823 when J.J. Berzelius succeeded in reducing K_2SiF_6 with molten potassium. There are two forms of silicon.

I. **Amorphous brown powder** of elementary silicon may be obtained by high temperature reduction of silica with magnesium or aluminium.

II. (i) **Crystalline silicon** is obtained by high temperature reduction of potassium silicofluoride, K_2SiF_6 with Al.



The excess of aluminium is removed with dilute HCl which leaves silicon unreacted.

(ii) Crystalline silicon is also made by the reduction of silica with high purity coke in an electric arc furnace; the SiO_2 is kept in excess to prevent the formation of SiC (a very hard abrasive and refractory material).

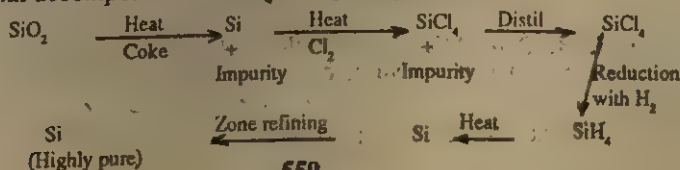


The reaction is frequently carried out in the presence of scrap iron (with low P and S content) to produce ferrosilicon alloys.

(iii) **Very pure form of crystalline silicon** is produced by the reduction of volatile SiCl_4 or a chlorosilane with exceedingly pure molten zinc, aluminium or magnesium at 1273K.



Thermal decomposition of SiH_4 also gives pure silicon.



Highly pure silicon is used as the starting material for the manufacture of semi-conductors for transistors, *etc.*

Recently a one step process has been developed to produce high purity silicon for solar cells. In this process, Na_2SiF_6 (a waste product of phosphate fertilizer industry) is reduced by metallic Na; the reaction is highly exothermic and is self sustaining without requiring any extra fuel.

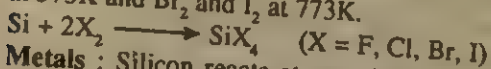
12.8.2 Properties of Silicon

It exists in two forms - amorphous (brown) and crystalline (blue grey with metallic lustre) - which are not true allotropic forms. The amorphous form is more reactive. Both the forms have diamond lattice (both differ in their particle size), but the silicon atoms are less closely packed than carbon. Its density, therefore, is only 2.4 g/cm^3 compared to 3.51 g/cm^3 for diamond. The pure metal is only poor electric conductor (semi-conductor) at room temperature, however, at increased temperature, the presence of crystal defects or impurities enhance the conduction significantly.

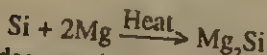
Chemical Reactions : Most of the reactions given below only refer to the amorphous form, since the crystalline variety is comparatively inert, except at high temperatures.

Halogens : Silicon reacts directly with halogens to produce tetrahalides.

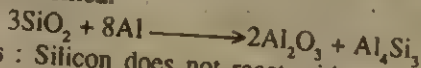
The reaction with F_2 is explosive at room temperature. Chlorine reacts at 573K and Br_2 and I_2 at 773K.



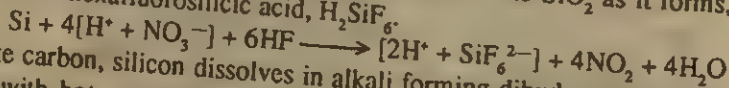
Metals : Silicon reacts at very high temperature (2000-3000K) with active metals, *e.g.*, Al, Mg, Ca, Zn, *etc.* producing silicides, which are analogous to carbides but more reactive. Silicon does not form binary compounds with Ge, Sn and Pb.



Silicides can be produced more economically directly from readily available silica.



Acids : Silicon does not react with acids except a mixture of nitric acid (an oxidizing acid) and HF which dissolves the SiO_2 as it forms, to produce hexafluorosilicic acid, H_2SiF_6 .



Unlike carbon, silicon dissolves in alkali forming dihydrogen and silicate; with hot aqueous alkali silicon gives orthosilicate and dihydrogen.

Cold or hot water has no action on silicon.

Some typical reactions of silicon and its extraction methods are given in Fig. 12.15.

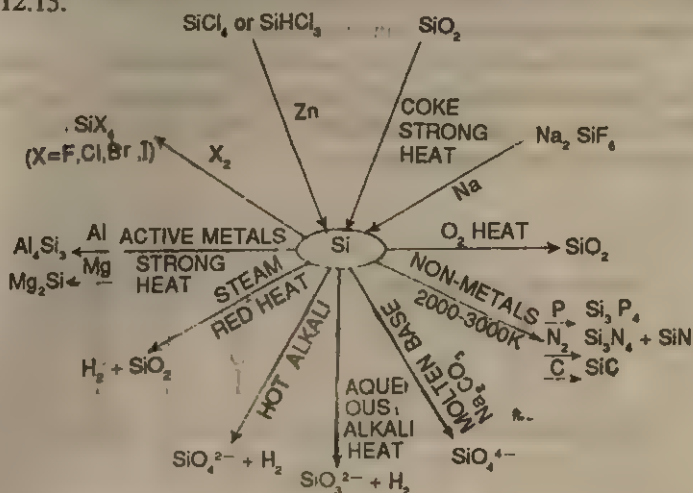


Fig. 12.15 some typical reactions of silicon and its extraction methods

12.8.3 Uses of Silicon

Silicon is used : (i) in the preparation of silicones, polymeric organosilicon compounds, (ii) to prepare components such as transistors, rectifiers, photocells and detectors because of its semi-conducting properties, (iii) in the preparation of carborundum, SiC which is used as an abrasive, and (iv) for reducing metal oxides (MgO) and to remove manganese and dioxygen from steel.

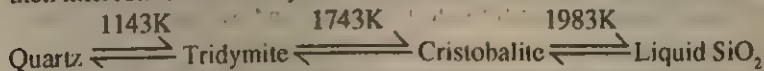
Ferrosilicon (Fe + Si) an alloy of silicon is used in the metallurgical industry to deoxidize steel, to manufacture acid and corrosion-resistant steel alloys.

Aluminium alloys for aircraft are strengthened with silicon. Silicon forms several alloys like silicon bronze, manganese silicon bronze, etc. which are very hard and have good tensile strength.

12.9 SILICA AND SILICATES

12.9.1 Silica

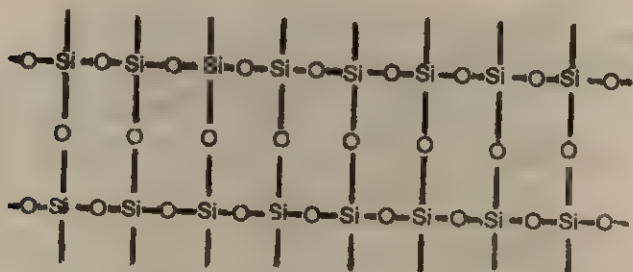
Silica, SiO_2 exists in three crystalline forms which are stable at different temperatures. These are (i) quartz, (ii) tridymite, and (iii) cristobalite. Thermodynamically, quartz is the most stable form. Since their interconversion is very slow, all the three forms are found in nature.



All the forms of silica possess three dimensional structure based upon SiO_4 tetrahedra in which each oxygen atom is common to two tetrahedra. In contrast, carbon dioxide is a discrete molecule with multiple bonds between carbon and oxygen. These silicon tends to form extended

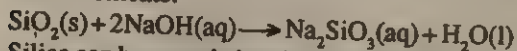
-Si-O-Si-O-chains and networks in contrast to carbon whose catenation depends upon the versatility and strength of C-C bonds. Stable silicon compounds hardly make use of multiple bonds.

Another form of silica, *i.e.*, stishovite, has different structure, the silicon having octahedral stereochemistry. Silica occurs in an amorphous form as flint and opal. Vitreous form of silica finds many uses in the laboratory. It is used to make glass ware.



Infinite three dimensional giant macromolecule of silica

Silicon (iv) oxide is much less reactive than carbon dioxide, but like that compound, it is an acidic oxide. Thus, SiO_2 on heating with concentrated sodium hydroxide solution or molten sodium hydroxide forms sodium silicate.



Silica can be regarded as the anhydride of $\text{Si}(\text{OH})_4$. It is insoluble in water and melts at 1973K to form a viscous liquid which on cooling forms glass (fused silica). Silica glass is used for the manufacture of vessels used in the laboratory and industry. Silica also reacts with fluorine and hydrofluoric acid. The reaction with hydrofluoric acid is used in qualitative detection of silica or silicates. Certain gems, *e.g.*, amethyst also consists of silica coloured by impurities.

12.9.2 Silicates

Silicate minerals and complex aluminosilicate clays are present in abundance in the earth's crust. Its weathered products, *e.g.*, soils, clays, and sand consist almost entirely of silicates and silica. The silicates are usually giant molecules rather like silica, but which contain many other metallic elements in addition to the silicon and oxygen. Quartz, mica, asbestos, feldspars and zeolites are all silicate minerals.

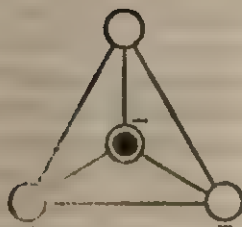
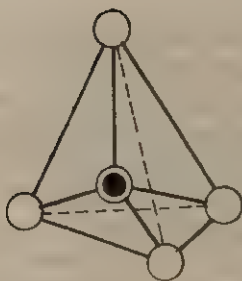
The vast majority of silicates are highly insoluble (only alkali metal silicates are water soluble). A common feature to all these complex silicate anions is SiO_4^{4-} tetrahedron, the basic structural unit.

These tetrahedra can exist either as discrete structural entities or can combine by corner sharing of oxygen atoms into larger units.

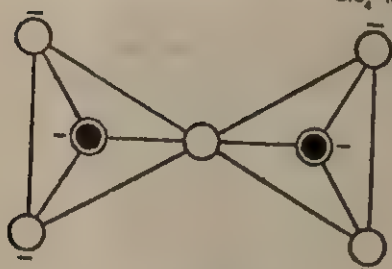
The resulting 'O' lattice is frequently close-packed or approximately so. Since these silicate rocks are electrically neutral, they must also contain a sufficient number of cations such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , Mn^{2+} to balance all the negative charges carried by the oxygen atoms. These cations, according to their size, occupy tetrahedral, octahedral or other sites present in the crystal lattice of silicates. The SiO_4 units can build up into chains, multiple chains (or ribbons), rings, sheets and three dimensional networks summarized in Table 12.9.

TABLE 12.9 Structural arrangement of SiO_4 units in various silicates

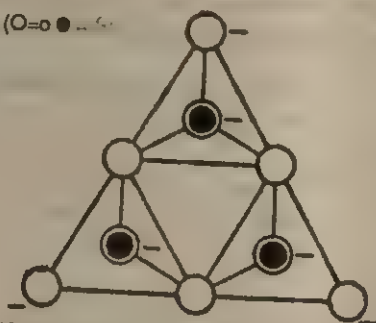
Structural arrangement	Anion unit	Example
(i) Discrete anions:	$(\text{SiO}_4)^{4-}$	Orthosilicates: Zircon, ZrSiO_4 ; Phenacite, Be_2SiO_5 ; Forsterite, Mg_2SiO_4
Two tetrahedra sharing one oxygen	$(\text{Si}_2\text{O}_7)^{6-}$	Pyrosilicates: Akemanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$
Closed rings of tetrahedra, each sharing two oxygens	$(\text{Si}_3\text{O}_9)^{6-}$ $(\text{Si}_6\text{O}_{18})^{12-}$	Cyclic silicate: Benitoite $\text{BaTiSi}_3\text{O}_9$ Beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$
(ii) Extended anions Continuous single chains of tetrahedra, each sharing two oxygens	$(\text{SiO}_3)_n^{2n-}$	Pyroxenes: Spodumene, $\text{Li Al}(\text{SiO}_3)_2$; Enstatite, $(\text{MgSiO}_3)_2$
Continuous double chains of tetrahedra sharing alternately two and three oxygens	$(\text{Si}_4\text{O}_{11})_n^{6n-}$	Amphiboles: Anthophyllite, $\text{Mg}_7(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$ Asbestos have these double chains
Continuous sheets of tetrahedra, each sharing three oxygens	$(\text{Si}_2\text{O}_5)_n^{2n-}$	Talc, $\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2$; Kaolinite $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$ Micas and clays belong to this class
(iii) Three dimensional networks	SiO_2	Cristobalite, SiO_2 Quartz, SiO_2 Felds par. e. g. $\text{NaAlSi}_3\text{O}_8$ orthoclase $\text{K}[\text{AlO}_2(\text{SiO}_2)_3]$ and the open framework zeolite also assume this arrangement.



SiO_4^{4-} ion (O=○ ●=Si)

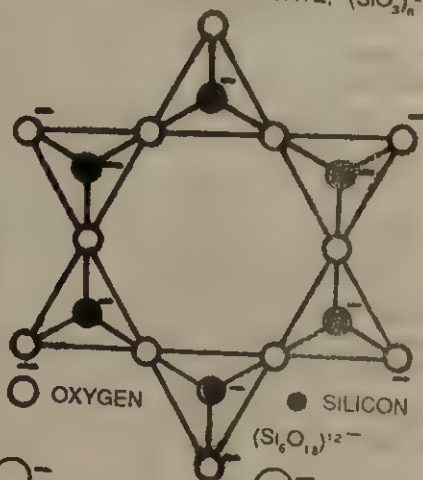


$\text{Si}_2\text{O}_6^{4-}$ (O=○ ●=Si)

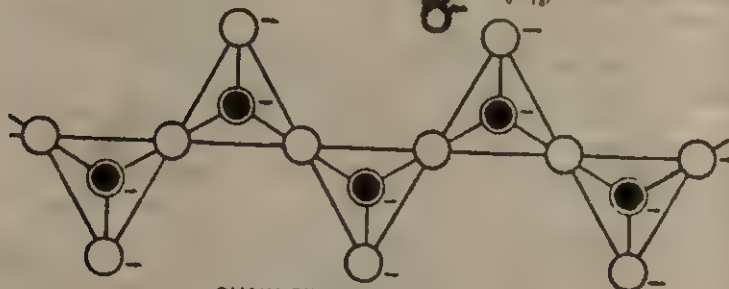


CYCLIC SILICATE, $(\text{SiO}_3)_n^{2n-}$ (O=○ ●=Si)

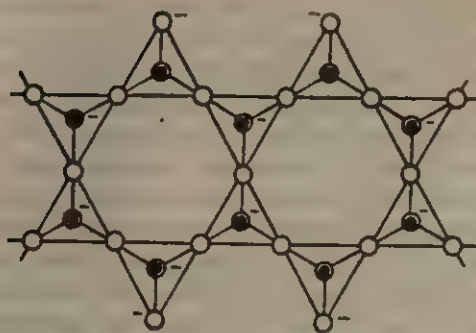
Structures of discrete
anions involving SiO_4
tetrahedra ;
● = Silicon
○ = Oxygen



$(\text{Si}_6\text{O}_{18})^{12-}$

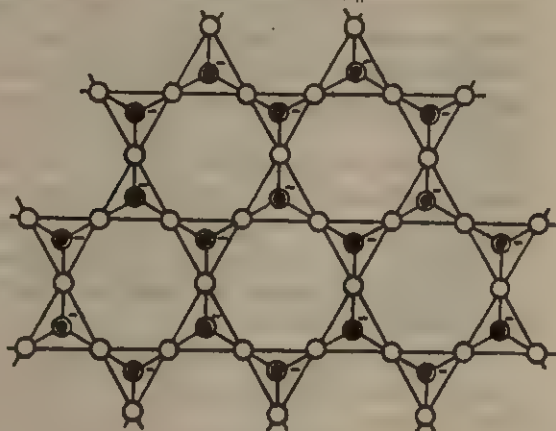


CHAIN SILICATE, $(\text{SiO}_3)_n^{2n-}$ (O=○ ●=Si)

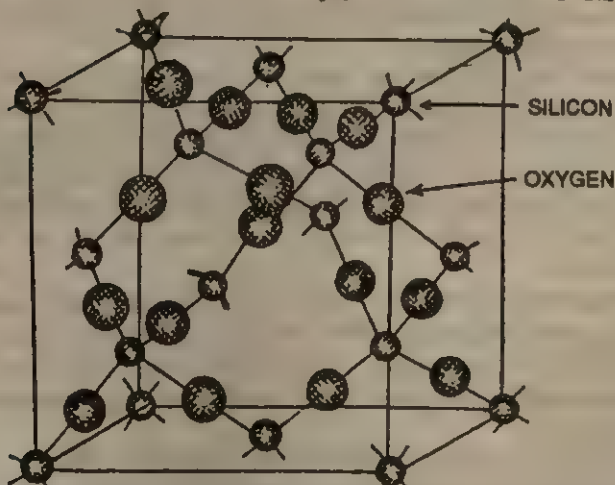


○ OXYGEN ● SILICON $(\text{Si}_2\text{O}_6)^{4-}$

Structures of extended
anions :
chains and sheets
of silicate tetrahedra ;
● = Silicon
○ = Oxygen



$(\text{Si}_2\text{O}_6)^{4-}$ ○ OXYGEN ● SILICON



Cristobalite (diamond like form of silica) : Representative structure of three dimensional networks of SiO_2 tetrahedra.

From Table 12.9 it is evident that the molecular formulae of some silicates contain metals other than silicon, *e.g.* Al, Ca, Mg, *etc.* This could be possible by the replacement of Si^{4+} by Al^{3+} ions to give aluminosilicates. As a result, the network will carry an overall negative charge which is counterbalanced by the incorporation of cations such as Na^+ and Ca^{2+} into the cavities in the structure. In this way, materials such as feldspars, *e.g.* orthoclase, $\text{K}[\text{AlO}_2(\text{SiO}_2)_3]$ and the open frame work zeolite structures are produced. Zeolites are three dimensional silicates, *e.g.*, analcite, (empirical formula $\text{Na}^+ [\text{Al Si}_2\text{O}_6]^- \text{H}_2\text{O}$). Zeolites can be used as ion exchangers, whose operation depends on replacing one kind of cation with another in these cavities. They are used in the treatment of hard water. Anhydrous zeolites are useful drying organic solvents and for adsorbing impurities from gases such as N_2 and H_2 . Because of this, they are called molecular sieves; the small H_2O molecules can get into the cavities but larger molecules cannot. The effective separation of straight chain alkanes from the branched chain or aromatic substances has been achieved by using zeolites.

Clays are aluminosilicates with the infinite sheets structure, and are usually colloidal in nature. Kaolinite is a clay widely used in making pottery. Asbestos is a fibrous silicate with either the chain or sheet structure *e.g.*, chrysolite, $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ has the sheet structure.

Micas have infinite sheet structure. Muscovite $\text{K}_2\text{Al}_4[\text{Si}_6\text{Al}_2\text{O}_{20}](\text{OH})_4$ is an example of mica.

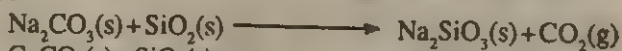
Glass and cement are the two well known synthetic silicates. Cement will be discussed in Unit 14.

12.9.3 Glass

Glass is the oldest man-made material. The Egyptians were familiar with a glass-like material as far back as 3000 B.C. After 1900 A.D. glass industry made rapid progress.

Glass is a complex mixture of an alkali metal silicate and various other silicates and is classified as a supercooled liquid, *i.e.*, liquid that has been cooled below its freezing temperature without crystallizing. Although it is solid, it flows slightly over a period of years. It is transparent to visible light, brittle and entirely lacking in the ordered internal structure characteristics of crystals. On heating, it gradually softens (no sharp melting point).

Ordinary soda glass is a mixture of sodium and calcium silicates. It is manufactured by heating together sand, soda ash (Na_2CO_3) and limestone (CaCO_3) at a temperature of about 1773K in a furnace. When the molten mass is cooled, it sets into a solid brittle glass. The reactions taking place are:



No definite formula is given to glass. The composition may be ap-

proximated to the formula $\text{CaSiO}_3 \cdot \text{Na}_2\text{SiO}_3 \cdot 4\text{SiO}_2$ (or $\text{CaO} \cdot \text{Na}_2\text{O} \cdot 6\text{SiO}_2$).

When sand is fused with sodium carbonate alone, a glassy mass known as "water glass" is obtained. It is soluble in water.

The limestone along with sand gives a glassy substance known as calcium silicate. It is insoluble in water but soluble in acids. Glass made from sand, soda ash and limestone is neither soluble in water nor in acids.

Molten glass, if cooled suddenly, it develops great internal strain and is likely to break into pieces. To avoid this, the molten mass must be cooled very slowly. This process of slow cooling is known as annealing. For every type of glass, there is a definite upper annealing temperature.

To produce coloured glass, small amount of other chemicals are added to the fused glass. The various chemicals used and the colour they impart are shown in Table 12.10

Glass is used for making jars, bottles and other vessels. Bottles and jars are made by machine in moulds. Window glass is made by flattening the soft hot glass between rollers and allowing it to cool slowly. We can produce many types of glasses (Table 12.11) by varying the ingredients.

Glass can be made into very fine threads. This is called fibre glass. It can be woven into a cloth which is very hard wearing and does not burn. The glass fibres can also be mixed with plastic to make a very light strong material. Car bodies and the hulls of boats are often made of fibre-glass.

TABLE 12.10 Substances used in the production of colour in glass

Substance	Colour imparted
1. Cobalt (II) oxide	Blue
2. Iron (II) compounds	Green
3. Iron (III) compounds	Yellow
4. Manganese dioxide	Violet
5. Chromium oxide	Green
6. Calcium fluoride	Milky
7. Uranium compounds (Sodium uranate)	Yellow
8. Colloidal gold (Gold chloride)	Red, purple, blue
9. Copper (I) oxide	Red, green, blue
10. Colloidal selenium	Ruby

TABLE 12.11 Properties and composition of various glasses

Type of glass	Composition	Properties	Uses
Soft or soda	75% SiO_2 , 15% Na_2CO_3 , 5% CaCO_3 , Remainder Al_2O_3 and MgO .	Inexpensive, common type	Bottles, jars, window panes, glass tubing
Hard or Potash	75% SiO_2 , 15% K_2CO_3 , 5% CaCO_3 , Remainder Al_2O_3 and MgO .		Laboratory glass ware
Flint	45% SiO_2 , 10% K_2CO_3 , 45% PbCO_3 .	Optically clean, high refractive index and high density	Electric bulbs, dinner wares, optical instruments, cut glass articles
Pyrex brand, Borosilicate	80% SiO_2 , 12% B_2O_3 , Remainder Na_2CO_3 and Al_2O_3 .	Thermally very stable, chemically inert	Laboratory glass ware, telescope lenses, etc.

12.9.4 Silicones

Silicones are polymeric organosilicon compounds containing individual or cross linked $-\text{Si}-\text{O}-\text{Si}-\text{O}-$ chains or rings in which some of the oxygens of SiO_4^{4-} tetrahedra are replaced by groups such as hydroxyl $-\text{OH}$, methyl $-\text{CH}_3$, ethyl, C_2H_5 , or phenyl $-\text{C}_6\text{H}_5$. They exhibit some of the properties of hydrocarbons and silicon oxygen compounds. They find many applications because of their remarkable stability to chemical attack or thermal decomposition. Depending on the relative molecular mass and extent of cross-linking, the polymers range from liquids to hard, thermally stable solids.

12.10 GROUP 15 ELEMENTS - GENERAL CHARACTERISTICS

Group 15 of the periodic table contains nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). The elements show the usual trends within the group. The metallic character increases as we go down the group. Thus, N and P are non-metals, As and Sb are metalloids and Bi is metallic. As usual, nitrogen is different from the other members. All the elements are characterized by $ns^2 np^3$ electrons in their valence shell which would suggest the formation of -3, +3 and +5 oxidation states and these are observed in P, As, Sb and Bi. Nitrogen, however, is found in every oxidation state between -3 and +5. Further in this group nitrogen is a gas and rest of the members of the group are all solids. Physical properties of nitrogen and phosphorus are listed in Table 12.12.

TABLE 12.12 Some physical properties of nitrogen and phosphorus

Property	Nitrogen	Phosphorus
Electronic structure	$[\text{He}]2s^2 2p^3$	$[\text{Ne}]3s^2 3p^3$
Covalent radius (pm)	70	110
Ionic radius, M^{3-} (pm)	171	212
Ionization energy (kJ mol^{-1})	Ist	1403
	IInd	2857
	IIIrd	4580
Electron affinity (kJ mol^{-1})	-31	60
Electronegativity	3.05	2.05
Density (g/cm^3)	0.88	1.82
Melting point (K)	63.2	316
Boiling point (K)	77.2	552
Oxidation states	-3, -2, -1	-3
	+1, +2, +3, +4, +5	+1, +3, +5
Physical state	Gas	Solid

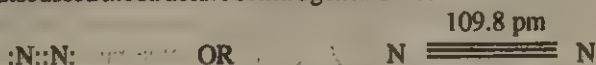
12.11 NITROGEN

Nitrogen was probably first recognized as a distinct gas by Rutherford in 1772. Lavoisier recognized its elemental nature on the basis of his work on combustion. He called the gas azote (Greek, a Zote = not life) as

it would not support life. But its name nitrogen was preferred because of its close relationship to nitre (Greek, nitron genon = nitre former).

Nitrogen is very much essential for all living organisms. Nitrogen present in the air dilutes oxygen and brings down its activity to safe limits. Nitrogen, in the combined form as proteins, is needed by plants and animals for the life process. It cannot be directly assimilated in the free state. The process of converting free atmospheric nitrogen into its useful compounds is called fixation of nitrogen (Fig. 12.16)

Nitrogen is a typical non-metal. It has five electrons in the valence shell. Nevertheless the maximum number of covalent bonds formed by nitrogen is limited to four (e.g. NH_4^+ salts) because it has only s and p orbitals in its valence shell. It is a diatomic molecule. It exists as discrete diatomic molecules in the gaseous, liquid and solid states. Two nitrogen atoms are combined by triple bonds with a bond distance of 109.8 pm and is very stable. Its bond dissociation energy is 946 kJ mol^{-1} . We have already discussed the structure of nitrogen in Unit 6.



Nitrogen has high electronegativity. Its value is next to that of fluorine and oxygen. It forms a variety of compounds which represent all the oxidation states ranging from -3 to +5, e.g., -3 (NH_3 , Mg_3N_2) + 3 (NaNO_2) and +5 (N_2O_5 , HNO_3).

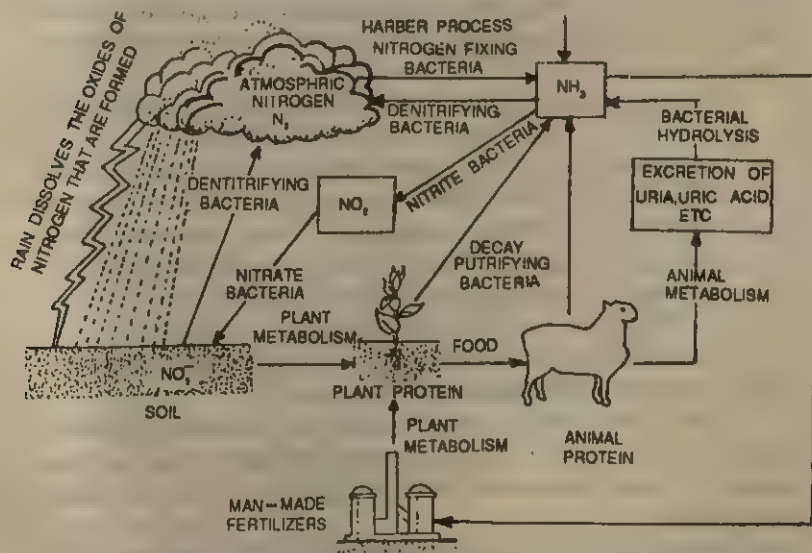


Fig. 12.16 Nitrogen is fixed naturally in thunderstorms and by the bacteria in the soil which are normally found in root nodules of some plants such as beans. Fertilizers contain artificially fixed nitrogen. Ammonia, manufactured by Haber's process is the main source of industrial nitrogen fixation. Ammonia is used for the manufacture of fertilizers.

12.11.1 Occurrence

Nitrogen occurs abundantly in nature in the free as well as combined forms. Molecular nitrogen makes up 78% by volume of the atmosphere. It is obtained from the atmosphere by liquefaction and fractionation. It is present in certain solid nitrate deposits, *e.g.*, as NaNO_3 in the earth's crust. Nitrogen is present in the amino acids from which animal and vegetable proteins are constructed. It also occurs in traces as ammonia in the atmosphere and is produced by the decay of organic matter and urine. In plants, animals, rock salts and mineral waters, nitrogen exists in the form of ammonium salts.

12.11.2 Preparation of Dinitrogen

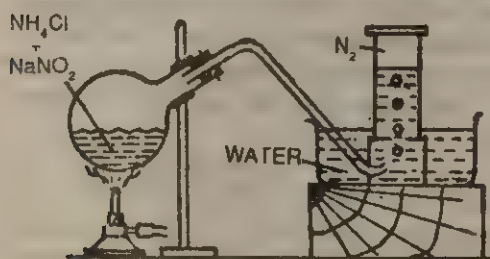


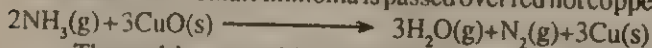
Fig. 12.17. Preparation of dinitrogen

Commercially dinitrogen is obtained by the fractional distillation of liquid air. Dinitrogen so produced contains a small amount of oxygen and noble gases. In the laboratory, dinitrogen is produced by heating sodium nitrite and ammonium chloride. These interact

to give ammonium nitrite, which then decomposes to give dinitrogen. Ammonium nitrite is so unstable that it cannot be stored. The gas is collected over water:



The assembly employed for the preparation of dinitrogen is given in Fig. 12.17. Small amounts of NO and HNO_3 are also formed in this reaction which are removed by passing the gas through aqueous sulphuric acid containing dichromate. Dinitrogen may also be prepared by the oxidation of ammonia. Ammonia is passed over red hot copper (II) oxide.



Thermal decomposition of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ also gives dinitrogen.

12.11.3 Properties and Reactions of Dinitrogen

Dinitrogen is a colourless and odourless gas. It is lighter than air and almost insoluble in water. Under standard conditions 100 mL of water dissolves 2 to 4 mL of dinitrogen. It is liquefied with difficulty. It is neutral towards litmus.

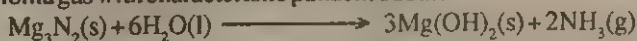
Dinitrogen is very stable and relatively inert. It is neither combustible nor a supporter of combustion. Combustion reactions are slowed down by the presence of dinitrogen in air.

1. **Reaction with metals:** Dinitrogen, however, combines with some preheated metals to form nitrides which are white solids and ionic in

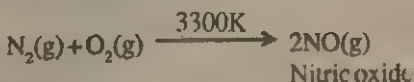
nature.



Nitrides decompose on reacting with water producing metal hydroxide and ammonia gas with characteristic pungent odour.

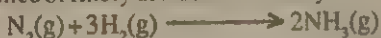


2. **Reaction with dioxygen:** Dinitrogen combines with dioxygen at 3300K to form nitric oxide in very small yield. Such high temperatures are produced by electric sparks.



Atmospheric dinitrogen and dioxygen also undergo this reaction during lightning. The reaction is reversible and is highly endothermic. Formerly this reaction was the basis of a method for the manufacture of nitric acid.

3. **Reaction with dihydrogen:** Dinitrogen combines with dihydrogen to give ammonia. The reaction takes place at 750K under high pressure in the presence of finely divided iron catalyst.



The reaction is reversible and exothermic. This reaction is the basis of Haber's process for the manufacture of ammonia.

Methods for the preparation of dinitrogen and some of its typical reactions are portrayed in Fig. 12.18.

12.11.4 Uses of Dinitrogen

1. The important uses of dinitrogen are based upon its inert nature. It is used : (i) for providing inert atmosphere in chemical process, (ii) to prevent the oxidation of easily oxidizable substances on exposure to air, (iii) for providing inert atmosphere in industries while handling gasoline and other inflammable liquids, (iv) in mercury thermometers for filling the space above mercury and thus, reducing the evaporation of mercury, (v) in the packing of foods (canned foods such as coffee, hydrogenated vegetable oils, etc., retain their flavour and colour much better if packed in the atmosphere of dinitrogen instead of air), and (vi) for filling in electric bulbs.

2. Dinitrogen is used in various processes for 'fixing' atmospheric nitrogen (Fig. 12.16).

3. It is used in the manufacture of nitrolime, calcium cyanamide ammonia, nitric acid and fertilizers.

4. Liquid dinitrogen is used as a coolant when low temperatures are required. It is also used as a refrigerant to preserve biological materials, in freezing food articles and in cryosurgery.

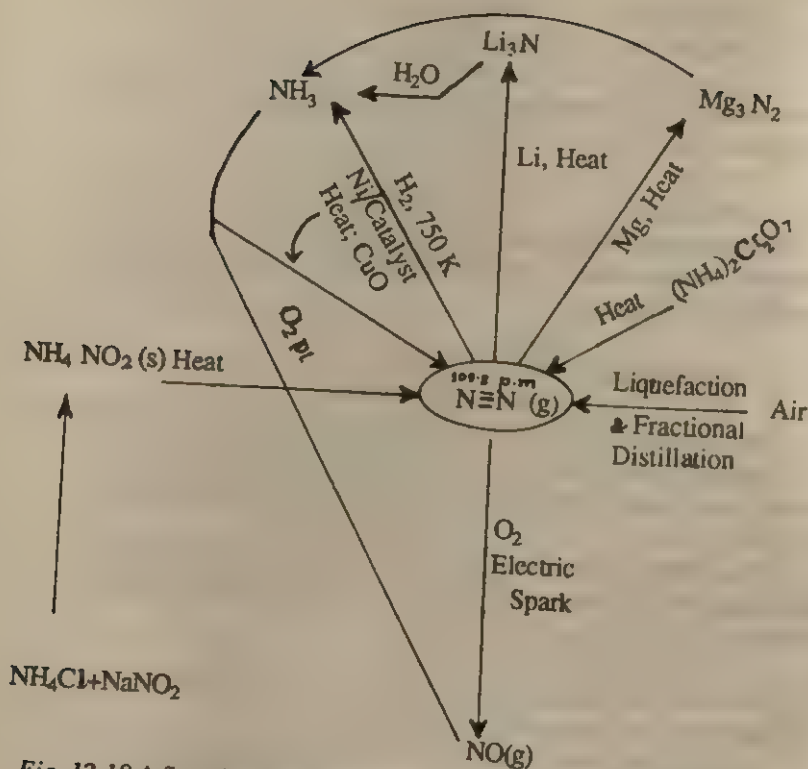


Fig. 12.18 A flow diagram illustrating the methods for the preparation of dinitrogen and its reactions

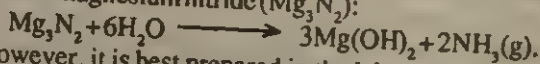
12.12 COMPOUNDS OF NITROGEN

Ammonia and nitric acid are amongst the important industrial chemicals. Their chemistry is discussed in the following pages. Oxides of nitrogen will also be taken up.

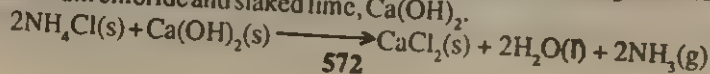
12.12.1 Ammonia

Ammonia is a very important compound for the fertilizer industry. It is present in atmosphere. Decaying of organic matters, e.g., horns and hoofs of dead animals and dead plants produce ammonia gas. It occurs in nature as ammonium chloride and ammonium sulphate which are found in some springs and earth's crust. The smell around toilets is also due to this gas.

Laboratory Preparation of Ammonia : Ammonia is produced by the hydrolysis of magnesium nitride (Mg_3N_2):



However, it is best prepared in the laboratory by heating a mixture of ammonium chloride and slaked lime, $\text{Ca}(\text{OH})_2$.



The apparatus used in the preparation of the gas is portrayed in Fig. 12.19. A finely ground mixture of ammonium chloride (1 part) and slaked lime (2 parts) is placed in a round bottom flask. On heating, ammonia is evolved. The gas is passed through quicklime (for drying) and collected by the downward displacement of air as it is lighter than air. It cannot be collected over water because it is highly soluble in water. Water is formed during the course of reaction. The flask is always positioned in a tilted fashion to avoid the condensed water drops which may trickle back on to the hot glass and crack it.

Sulphuric acid and anhydrous calcium chloride cannot be used for drying as both react with ammonia.

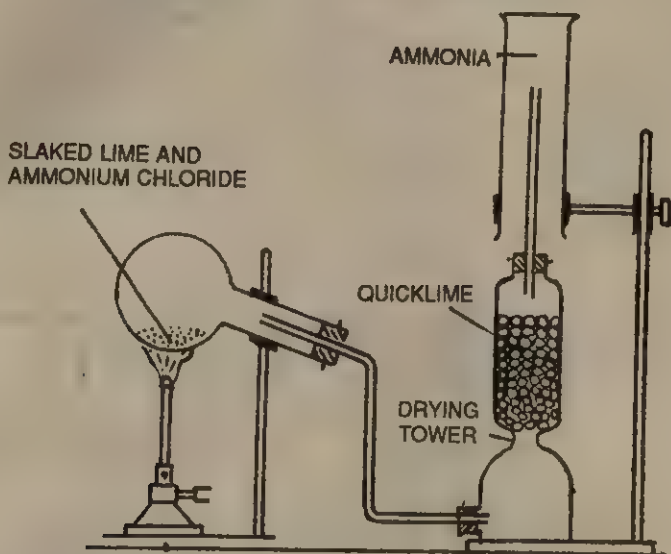
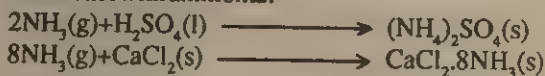


Fig. 12.19 Laboratory preparation of ammonia.

Manufacture of Ammonia

Ammonia is manufactured by the direct combination of dinitrogen and dihydrogen under suitable conditions. This reaction was discovered by a German chemist, Fritz Haber in 1908 and is called the Haber's process.



Dinitrogen is obtained by fractional distillation of liquid air and dihydrogen is obtained from natural gas or by the Bosch's process. The two gases are dried and mixed in the ratio of 1 : 3 by volume.

The reaction is reversible, exothermic and proceeds with a decrease in volume. Hence, according to Le Chatelier's principle, high pressures and low temperatures should give better yield. At low temperatures, however, chemical reactions proceed slowly. In practice, an optimum

temperature of 773K and a pressure of 250 - 1000 atm are employed. A mixture of two gases compressed to 250-1000 atm is passed over finely divided iron or iron oxide (catalyst) heated to 773K. Alumina or molybdenum (promoter) is added to increase the rate of attainment of equilibrium. The products are passed through a cooling chamber (Fig. 12.21). Ammonia, under high pressure, then liquefies and can be separated. Only 10% conversion occurs. Figure 12.20 shows a flow diagram for the modern Haber's process.

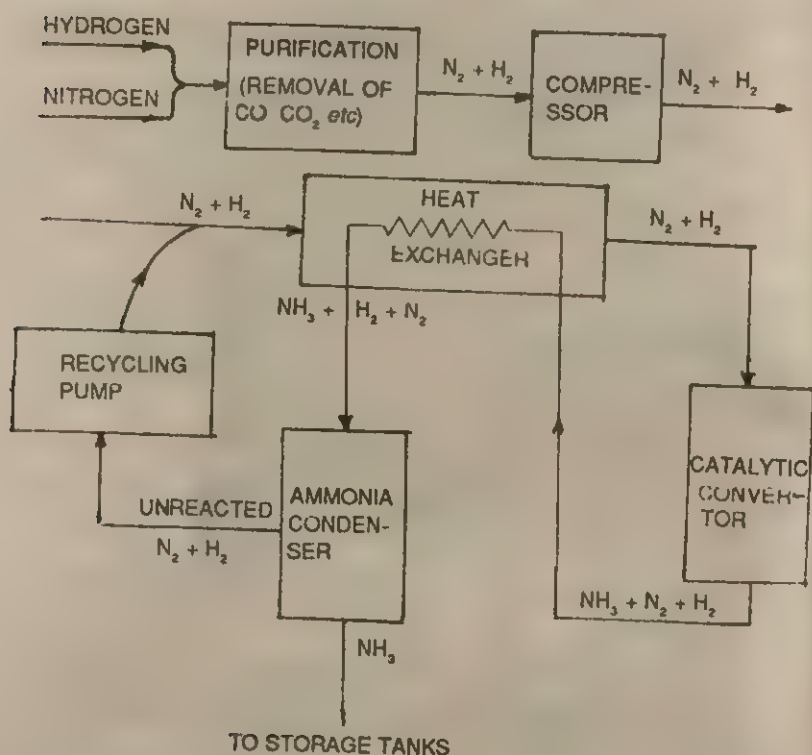


Fig. 12.20. A flow diagram for the Haber's process.

Properties of Ammonia : Ammonia is a colourless gas with a characteristic choking smell. It is lighter than air. It can be easily liquefied to a liquid (b.p. 240K). Its melting point is 198.4K.

Ammonia is a trigonal pyramidal molecule with polar nature. In the solid and liquid forms, it is associated through extensive hydrogen bonding because of the high electronegativity of nitrogen. This additional bonding explains the exceptionally higher melting and boiling points of ammonia

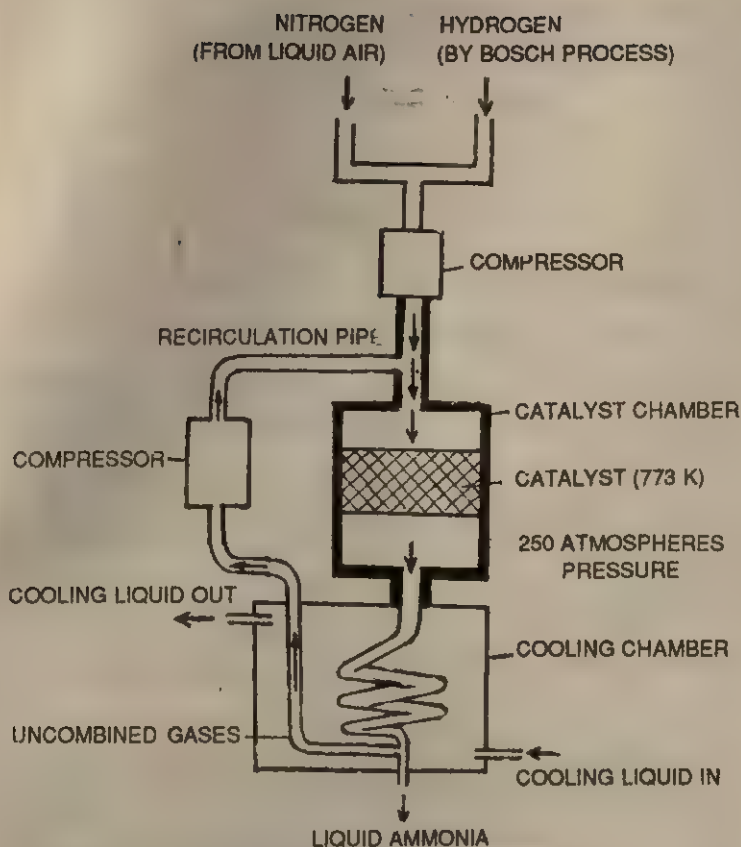
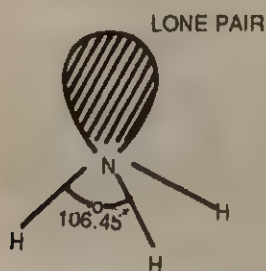


Fig.12.21 Manufacture of ammonia by Haber's process.

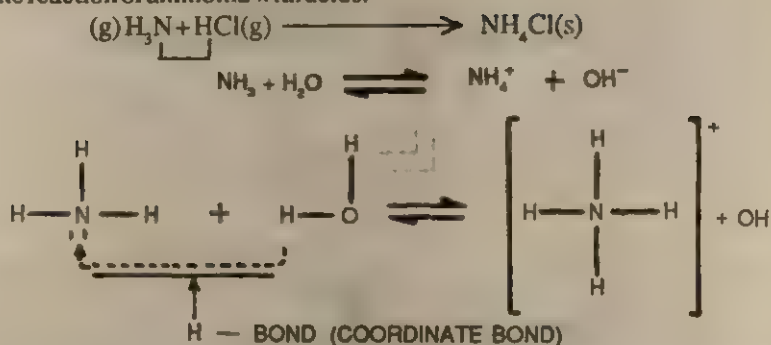


compared to those of the other hydroxides of group 15 (Unit 6). It dissolves in water to give an alkaline solution. Its high solubility is attributed to the presence of H-bond.

The reaction of ammonia with water is the donor-acceptor interaction. The ammonia molecule, because of the presence of a lone pair of electrons, is the donor (Lewis base) and the proton eliminated from the water molecule is the acceptor of (Lewis

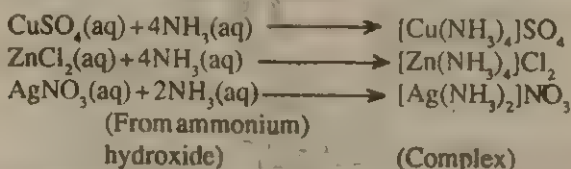
acid) a lone pair of electrons from nitrogen. The donor property of NH_3 is also visible in its other properties, e.g., the attachment of protons during

the reaction of ammonia with acids.

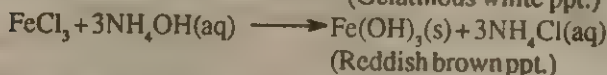
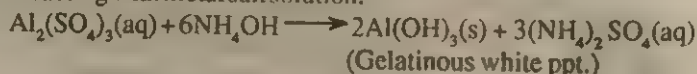


Complex formation : Ammonia forms co-ordinate bonds with metal ions by donating its lone pair of electrons. Such complexes find use in qualitative analysis.

On adding ammonia or ammonium hydroxide solution to salt solutions of metals such as Cu, Zn and Ag, metal hydroxides are formed which dissolve in excess of ammonia to form soluble ammine complex ions.



The dissolution of NH_3 in water is a reversible reaction. Only a small proportion of dissolved ammonia is present in solution in the form of NH_4^+ ions while most of it is contained as NH_3 . Ammonia water, therefore, gives smell of ammonia. It neutralizes acid solution to produce ammonium salts. The OH^- ions present in its water solution form insoluble metal hydroxides on reacting with metal salt solution.



These reactions are used to identify the metal ions in the qualitative analysis.

Combustibility : Ammonia does not burn in air. It, however, burns in dioxygen with a greenish flame.



In the presence of heated platinum catalyst, ammonia is oxidized to nitric oxide, which immediately combines with atmospheric oxygen to give brown coloured nitrogen dioxide gas. This reaction is used in the manufacture of nitric acid from ammonia.

Reducing properties : (i) Ammonia reduces heated metallic oxides of less

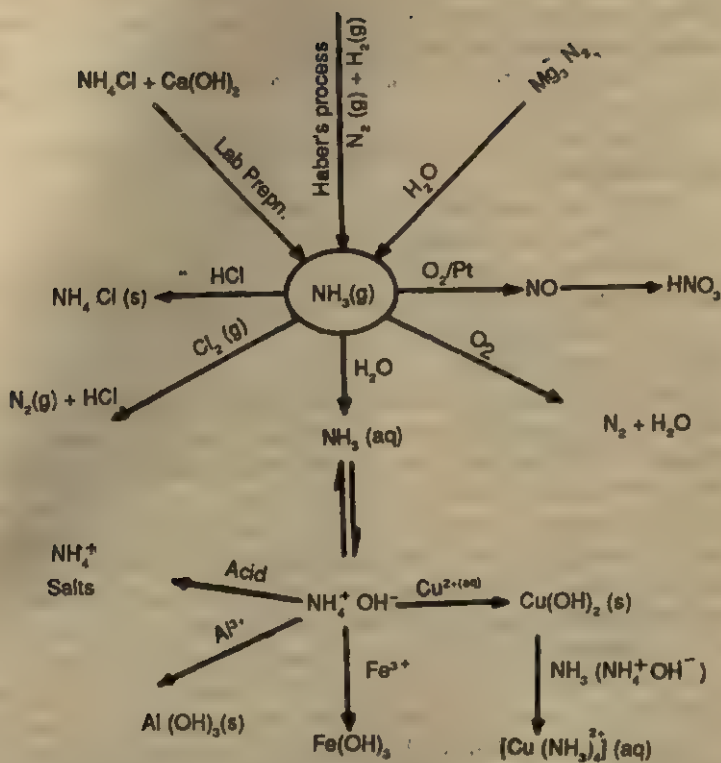
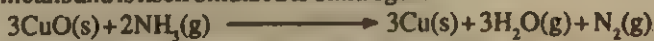
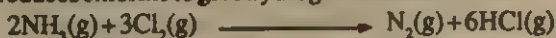


Fig. 12.22 A flow chart illustrating the preparation of ammonia and its reactions.

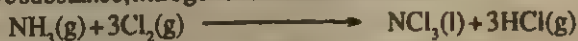
reactive metals and is itself oxidized to dinitrogen.



(ii) It reduces chlorine to give hydrogen chloride.



The hydrogen chloride, thus, formed combines with excess of ammonia producing dense white fumes of ammonium chloride. This reaction is used to detect ammonia gas. If excess of Cl_2 is used, a highly explosive substance, nitrogen trichloride is formed.



Methods for the preparation of ammonia and its typical reactions are summarized in Fig. 12.22

Uses of Ammonia: Ammonia is used:

1. In the manufacture of various fertilizers, such as ammonium sulphate, ammonium phosphate, ammonium nitrate, urea, etc.
2. In the manufacture of nitric acid (Ostwald's process), sodium cyanide, ammonium chloride (used in dry cells, Leclanche cells and

preparing digestive medicines), ammonium nitrate (used in making explosives and in the manufacture of calcium ammonium nitrate, CAN), ammonium carbonate (used in baking powders), *etc.*

3. In Solvay's process for the manufacture of sodium carbonate and sodium bicarbonate.

4. In the manufacture of polyamide plastics and many organic chemicals and wood pulp.

5. In the manufacture of artificial silk (rayon).

6. As a refrigerating agent in ice-plants.

7. Ammonia-water solution is used for removing grease stains. The solution is also used for cleaning window panes, porcelain tiles, *etc.*

8. In household detergents.

12.12.2 Oxides of Nitrogen

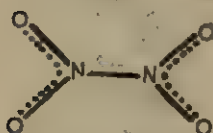
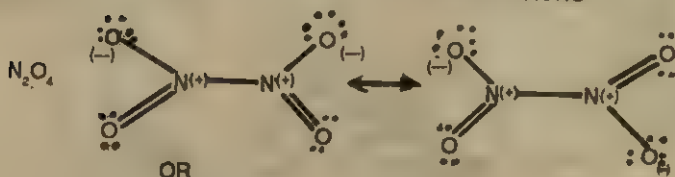
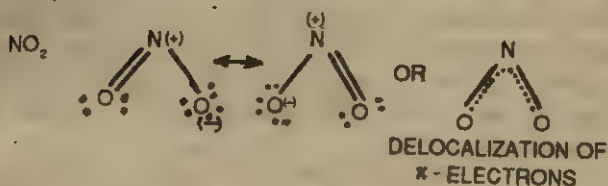
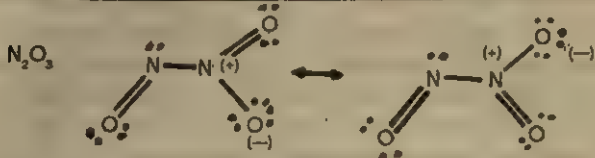
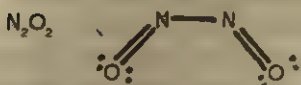
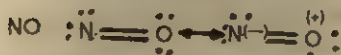
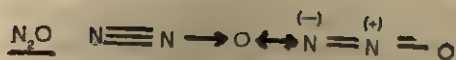
Oxides of nitrogen present a good study material with regard to their varied structures and diverse chemical behaviour as compared to the oxides of the other members of the nitrogen group. The oxidation states expected of nitrogen (ns^2np^3), would be -3 to $+5$. Nitrogen assumes only positive oxidation states with oxygen because oxygen is more electronegative than nitrogen. The ability of nitrogen to form multiple bonds to oxygen causes its oxides to be small molecules, not solid polymeric substances with simple M-O bonds as in the case of P, As, *etc.* Nitrogen-oxygen chemistry is rather complex. We shall here present a mere outline to give the students a feeling for the behaviour of the nitrogen atom in different environments. Table 12.13 lists the oxides of nitrogen with their physical states. Their structures are given in Fig. 12.23.

Dinitrogen oxide, N_2O and nitrogen oxide, NO are neutral, and the other oxides increases in acidity, $N_2O_3 < NO_2 < N_2O_5$.

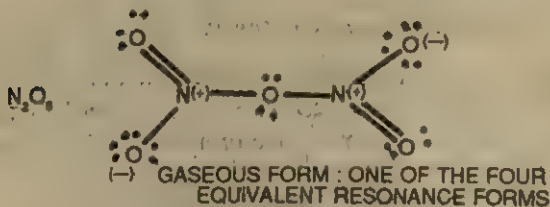
TABLE 12.13 Oxides of nitrogen

Oxidation state	Oxide formula	Name	Physical state at 298K
+1	N_2O	Dinitrogen monoxide (Nitrous oxide)	Colourless gas
+2	NO	Nitrogen monoxide (Nitric oxide)	Colourless gas
+2	N_2O_2	Dinitrogen dioxide	Solid
+3	N_2O_3	Dinitrogen trioxide	Deep blue liquid
+4	NO_2	Nitrogen dioxide	Brown gas
+4	N_2O_4	Dinitrogen tetraoxide	White solid
+5	N_2O_5	Dinitrogen pentaoxide	White solid

Both nitrogen monoxide and nitrogen dioxide are used in the manufacture of nitric acid. Dinitrogen tetraoxide has found its use as



TWO OF THE FOUR EQUIVALENT
STRUCTURES



$[\text{NO}_2^+]$ $[\text{NO}_3^-]$
SOLID IONIC FORM

Fig. 12.23 Structures of the oxides of nitrogen.

an oxidant for rocket fuels in missiles and space vehicles. Dinitrogen oxide is used for anaesthetic purposes. Nitric oxide is one of the atmospheric pollutants emitted during the burning of oil and coal (in power stations, refineries and automobiles).

12.12.3 Nitric Acid

Nitric acid was known as 'aqua fortis' (strong water) to the early alchemists because of its corrosive action on many substances. In 1658, Glauber prepared it using sulphuric acid and potassium nitrate (a present laboratory method). Traces of free nitric acid are found in rain water after thunderstorm and lightning. Lightning initiates the combination of atmospheric dinitrogen and dioxygen to give nitric oxide which combines with more of dioxygen to produce nitrogen dioxide. Nitrogen dioxide dissolves in rain water to produce nitric acid. It is widely distributed in nature in the form of its salts, viz, sodium nitrate, potassium nitrate and calcium nitrate.

Laboratory Preparation of Nitric Acid : Nitric acid is prepared by heating gently a mixture of sodium (or potassium) nitrate and concentrated sulphuric acid in a glass retort. The vapours of nitric acid evolved are condensed as a light yellow liquid in a receiver cooled under tap water (Fig. 12.24)

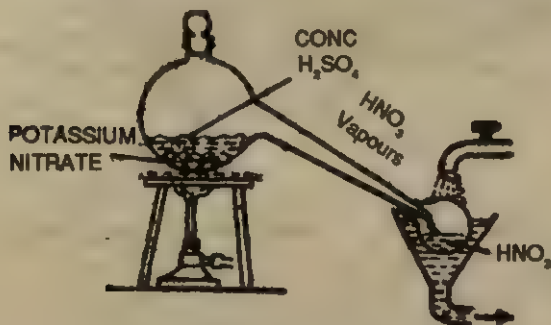


Fig.12.24 Preparation of nitric acid.

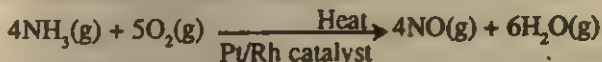
Pure nitric acid is, however, a colourless liquid. The yellow colour is due to the dissolved nitrogen dioxide in the acid. This gas is often produced due to the decomposition of nitric acid by the heat of reaction.



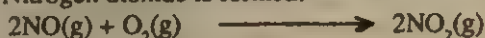
This is why gentle heating is advised.

Manufacture of Nitric Acid : Nitric acid is produced by the catalytic oxidation of ammonia (Ostwald's process). A mixture of purified air (10 parts by volume) and ammonia (1 part by volume) is passed

through a chamber containing platinum gauze at 1000-1100K (Fig. 12.25). Ammonia is then oxidized to nitric oxide.



The reaction is exothermic and the heat of the reaction maintains the required temperature of the catalyst chamber. The hot gases are rapidly cooled by passing through a large empty chamber. Nitric oxide does not combine with dioxygen in the air until it is cooled to ~323K. Nitrogen dioxide is formed.



The nitrogen dioxide, mixed with excess of air, is then absorbed in water to give HNO_3 .

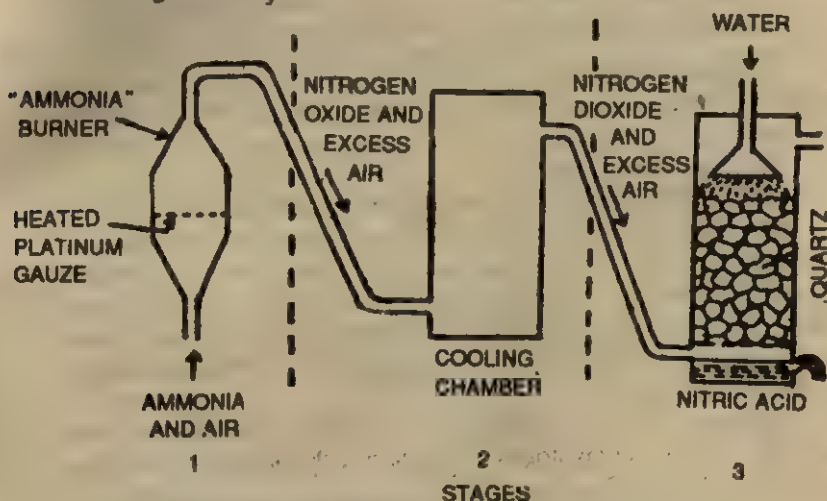


Fig. 12.25 Manufacture of nitric acid

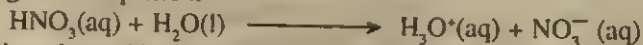


Properties of Nitric Acid : Pure nitric acid is a colourless, fuming and highly corrosive liquid. It attacks the skin leaving yellow stains. It boils at 357.3K. It freezes to a white solid at 231.4K. Its density is 1.504 g/cm³. Concentrated nitric acid is often yellow due to dissolved nitrogen dioxide produced by its photochemical decomposition.

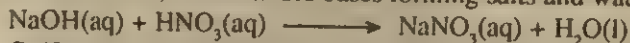
The so called commercial concentrated nitric acid (16M) contains about 70% by mass of pure acid and 30% water. It has a specific gravity of 1.414. It can be concentrated to 98% by dehydration with conc. H_2SO_4 . Anhydrous acid can be obtained by distilling conc. aqueous acid with phosphorus pentoxide under low pressure.

1. **Acidic properties:** It is soluble in water in all proportions. The aqueous solution is stable and shows acidic properties. In aqueous

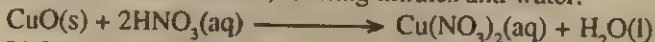
solution, nitric acid is very strong acid and ionizes almost completely according to the equation.



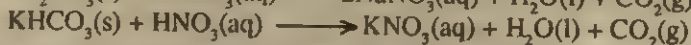
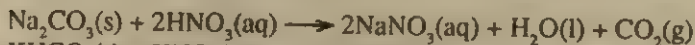
(ii) Like other acids, it neutralizes bases forming salts and water.



(iii) It reacts with basic oxides, forming nitrates and water.



(iv) It reacts with carbonates and bicarbonates liberating carbon dioxide



2. **Oxidizing properties :** Nitric acid behaves as an oxidizing agent whether it is concentrated or dilute. The following reactions illustrate its oxidizing nature :

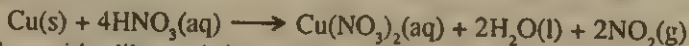
(a) **Reaction with metals**

Nitric acid reacts with all metals except gold and platinum. Its reaction with many metals is slowed down because it renders the surface passive. Aluminium is not attacked by the acid as its surface remains covered by a thin layer of aluminium oxide. Iron and chromium are made passive by the acid. The reaction products formed depend upon the concentration of the acid, the activity of the metal and the temperature.

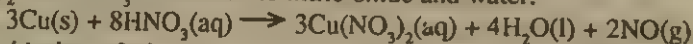
(i) **Oxidation of magnesium and manganese :** Very dilute nitric acid (say 5%) gives dihydrogen on reacting with magnesium and manganese at ordinary temperature.



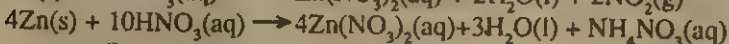
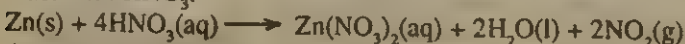
(ii) **Oxidation of copper :** With concentrated acid copper is oxidized to copper (II) nitrate and the nitric acid is reduced to nitrogen dioxide and water.



Also with dilute nitric acid (~ 50%) copper is oxidized to $\text{Cu}(\text{NO}_3)_2$ but HNO_3 is reduced to nitric oxide and water.



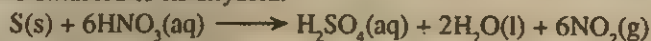
(iii) **Oxidation of zinc :** A number of reduction products NO_2 , NO , N_2O , N_2 or NH_4NO_3 are formed when the active metals such as zinc react with HNO_3 .



(Very dilute)

(b) Reaction with non-metals

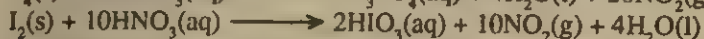
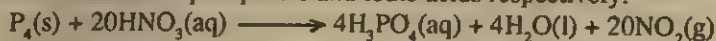
(i) **Oxidation of sulphur** : Powdered sulphur reacts with hot concentrated nitric acid to give dense brown fumes of nitrogen dioxide. Sulphur is oxidized to its oxyacid.



(ii) **Oxidation of carbon** : Hot concentrated nitric acid oxidizes carbon to CO_2 .

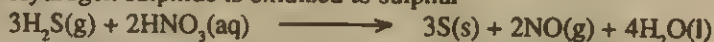


(iii) **Oxidation of phosphorus and iodine** : Both phosphorus and iodine are oxidized to phosphoric and iodic acids respectively.



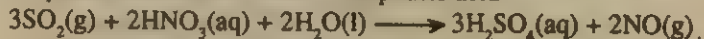
(c) **Reaction with inorganic compounds** : Concentrated (or dilute) nitric acid oxidizes many inorganic compounds and is itself reduced to nitric oxide.

(i) Hydrogen sulphide is oxidized to sulphur



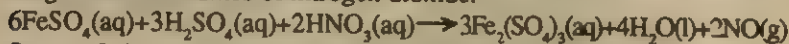
To a saturated solution of H_2S a few drops of concentrated HNO_3 is added. Hydrogen sulphide is oxidized to sulphur which precipitates and starts floating on the upper surface of the solution.

(ii) Sulphur dioxide is oxidized to sulphuric acid



(iii) Green coloured iron (II) sulphate is oxidized to orange coloured iron (III) sulphate.

The nitric acid is reduced to nitric oxide which on reacting with air gives brown fumes of nitrogen dioxide.



Some of the typical reactions of nitric acid are summarized in Fig. 12.26

Test of Nitric acid (or Nitrates)

1. Concentrated nitric acid on strong heating gives nitrogen dioxide and dioxygen. Nitrogen dioxide is recognized by its brown colour. Dioxygen reignites a glowing splint.

2. When some copper turnings are put in conc. nitric acid contained in a test tube and heated, dense brown fumes of nitrogen dioxide are evolved.

3. **Brown ring test.** To a cold solution of dilute nitric acid (NO_3^- ion) freshly prepared ferrous sulphate solution is added and then concentrated H_2SO_4 is added slowly along the walls of the tube. Acid forms the lower layer (denser than aqueous solution of $FeSO_4$). On the junction of the two layers a brown ring appears. Some heat is produced which is sufficient to initiate the reduction of NO_3^- ion to NO (forms a brown complex with $FeSO_4$). On stirring the solution, the

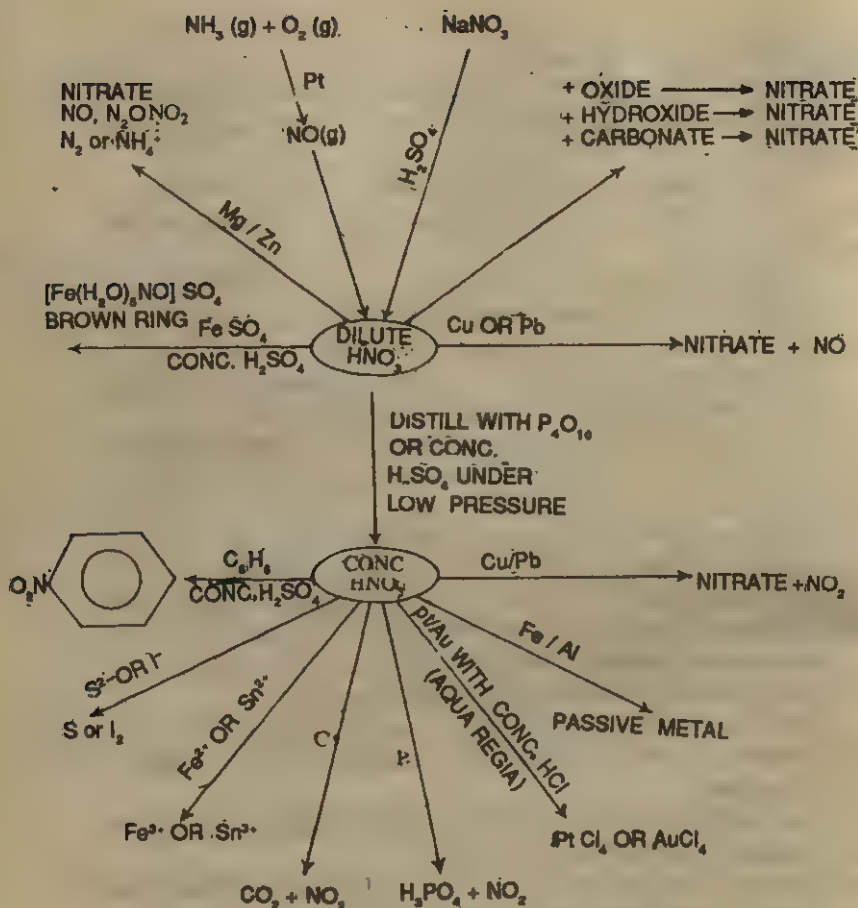
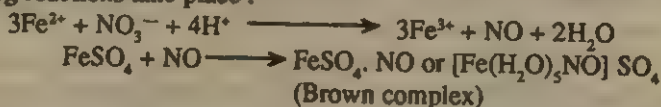


Fig. 12.26 Reactions of nitric acid

ring disappears as a result of heat produced during mixing of H_2SO_4 with aqueous solution and the whole solution becomes black. The following reactions take place :



Uses of Nitric Acid : Nitric acid is chiefly used as given below :

1. In the manufacture of fertilizers (ammonium nitrate and calcium ammonium nitrate), explosives (nitroglycerine, dynamite, TNT, picric acid, gun cotton), dyes, plastics, drugs, perfumes, textiles (cotton, wool and linen) synthetic fibres, photographic films.
2. In the extraction of certain metals.
3. In the refining of certain metals, e.g., Ag and Au.
4. In industries producing artificial silk and cellulose nitrate.

5. In the manufacture of chemicals, *e.g.*, phosphoric acid from phosphorus and oxalic acid from carbohydrates.
6. In the manufacture of different nitrates which are used as fertilizers, and in some medicines, photography and fireworks.
7. As a laboratory reagent.

8. For etching designs or names upon metals like copper, brass and bronze.

Structure of Nitric acid : The vapour of nitric acid consists of planar molecules which have the structure given in Fig. 12.27. In solid state, HNO_3 assumes the planar structure but with different dimensions.

The nitrate ion, NO_3^- is isoelectronic with carbonate ions, CO_3^{2-} and is also planar. The resonance structures of the NO_3^- are given in Fig. 12.27.

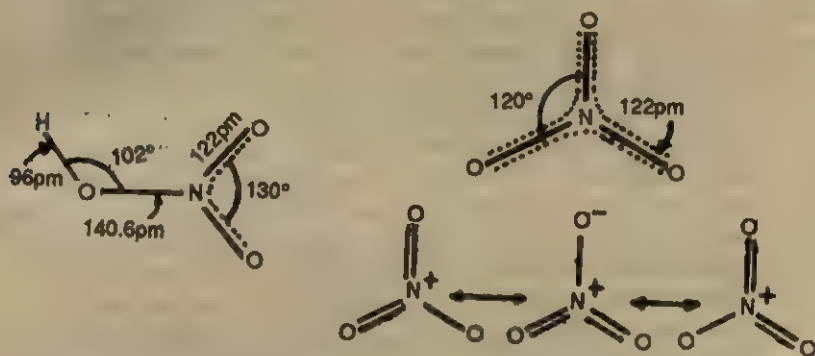


Fig. 12.27 Structure of HNO_3 in the gaseous state.

Resonance structures of the NO_3^- ion

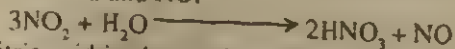
SMOG

The word smog refers to smoke-laden fog which reduces visibility to zero and seriously affects the respiratory organs. Smog is liable to occur when air near the earth is cooled below the dew point temperature. Because of this, air pollutants (smoke, sulphur dioxide, dust particles, *etc.*) get trapped in still air which cannot move upwards. The tropospheric temperatures, decreasing with altitude permits warm and less dense surface air to rise and carry away pollutants. These pollutants continue to hang in the atmosphere and form a layer of warm air over cooler surface air. During such a temperature inversion, the surface air is trapped and pollution level increases. Such conditions are prevalent in industrial townships and cities during winter season. Thus, it is a product of a damp climate and smoke and sulphur dioxide produced by the burning of coal for heat and power.

The word 'smog' has penetrated into the culture of metropolitan cities like Delhi, Calcutta, Bombay, *etc.* and industrial towns like,

Kanpur, Ahmedabad, etc. This is caused by exudate or waste from industries, e.g., ash, smoke etc. Other pollutants which also add to smog has specific origin, e.g. dust from cement factory, dust from metallurgical plants, etc. Automobile exhausts is also one of the major causes of smog.

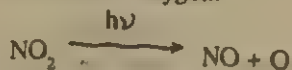
Now a new word has been put along with smog to characterize a different type of smog, i.e., 'photochemical smog', the product of a combination of automobile exhaust and sunny climate. Dinitrogen and dioxygen present in air combine with each other in high temperature regions in and around automobile engines, furnaces of coal or oil burning electric-power plants to produce colourless nitric oxide gas. In the presence of dioxygen it gets further oxidized to give brown coloured nitrogen dioxide gas. Both NO and NO₂ are quite reactive and do considerable damage to plants and animals. Nitrogen dioxide reacts with water vapours present in the air to produce corrosive droplets of nitric acid and NO.



Nitric acid is also produced by the dissolution of NO₂ gas (hanging in air) in rain water. This acid may react with traces of ammonia in the air to form solid ammonium nitrate, a pollutant.

The problem is further accentuated in areas with warm dry climates, conducive to light induced reactions (photochemical reactions).

Nitric oxide gas continues to get oxidized into nitrogen dioxide which often hangs over the city. Nitrogen dioxide, available at very low altitude, is a health hazard. It attacks lungs and may cause bronchitis and cancer. Its increasing concentration is likely to produce dangerous products. Nitrogen dioxide decomposes in the presence of sunlight to give NO and atomic oxygen.



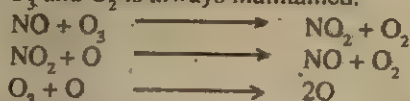
Atomic oxygen, in turn, reacts with dioxygen to give ozone. Ozone is a potential health hazard. Being oxidant in nature, it reacts destructively with many materials, e.g., rubber, paint and vegetation, etc. It affects eyes and lungs. Further it reacts with the unburnt hydrocarbons that are released into the atmosphere from automobile exhaust, and thus, produces dangerous products like organic peroxides and peroxyacetyl nitrates (PAN) which irritate eyes and damage the vegetation kingdom.

Efforts are on whereby the concentration of NO could be reduced in atmosphere close to earth.

The photochemical smog is confined to the region in which many photochemical oxidants are produced. It takes several hours for

a photochemical reaction of this nature to occur and by then considerable distances may be covered by air mass.

The reaction between naturally formed nitric oxide and O_3 is a normal occurrence in the upper part of the atmosphere. Somehow a balance between O_3 and O_2 is always maintained.



Further increase in the concentration of NO will increase the rate of conversion of ozone into dioxygen and could reduce the equilibrium level of ozone. Nitrogen oxide produced at low altitudes does not pose any threat to the ozone layer. But at high altitude, if enough NO is available, it would deplete the ozone to the point, that harmful effects on earth may become visible.

Thus, a photochemical smog may be defined as a brownish smog occurring in the city's atmosphere receiving large enough amounts of sunlight. It is caused by photochemical (light induced) reactions among nitrogen oxides, sulphur oxides, hydrocarbons, and other components of polluted air which produce photochemical oxidants.

12.13 PHOSPHORUS

Phosphorus was recognized in 1669 by Brand. Its name has been derived from its unique property of 'glowing' in the dark (phosphorescence).

Phosphorus, like nitrogen, is needed by all living beings because it enters the composition of some proteins (both vegetable and animal proteins). It is an essential fertilizer for plants.

Phosphorus is a typical non-metal. Its valence shell contains 5 electrons. Phosphorus atoms unite into diatomic P_2 , tetratomic P_4 and polymeric P_n molecules. P_2 molecules have a structure similar to that of N_2 and exist only above 1073K. In the liquid or vapour form P_4 molecules are stable below 1073K.

As seen in other groups, phosphorus differs from nitrogen in many respects. This is ascribed to the difference in their sizes and electronegativity values. Some of the points are listed below :

- The strong $N \equiv N$ bond and absence of catenation; phosphorus exists as P_4 , each atom joined by single bonds.
- Nitrogen is limited to a maximum co-ordination number of four (absence of d orbitals) whereas phosphorus can expand its valence shell to accommodate a coordination number of six.
- Nitrogen takes part in hydrogen bonding. The difference in the physical properties of NH_3 and PH_3 is due to hydrogen bonding
- Oxides of nitrogen are small molecules, whereas oxides of phos-

phorus are solid and polymeric substances with single P — O bonds. This is because nitrogen can form multiple bonds to oxygen.

(e) Molecular nitrogen is unusually inert because of its high bond dissociation energy (946 kJ mol^{-1}).

(f) Nitrogen forms numerous compounds with sp and sp^2 hybridizations. Such hybridizations are not seen in the compounds formed with phosphorus.

12.13.1 Occurrence

Phosphorus is found in the form of phosphate deposits in the crust of the earth. Its common minerals are phosphorite, $\text{Ca}_3(\text{PO}_4)_2$ fluoroapatite, $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$ or hydroxyapatite, $\text{Ca}(\text{OH})_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$.

Phosphorus is an essential constituent of bones, teeth, muscles, brain and nerve tissues (DNA).

In plants, phosphorus is contained chiefly in the seed proteins. The bones of animals (phosphorus as hydroxyapatite) and rock phosphates are the main sources of phosphorus.

Immense deposits of phosphates are found in North Africa, North America, on the Nauru and Ocean Islands in the Pacific and in the Kola Peninsula in the USSR. Phosphate deposits are also found in Rajasthan (India).

12.13.2 Allotropy in Phosphorus

Phosphorus exists in several allotropic forms of which only three are important. These are white or yellow, red and black phosphorus. White phosphorus exists as P_4 molecules (tetrahedral). Red phosphorus has a polymeric type of structure resulting from the partial breakdown and interlinking of P_4 tetrahedra units to give P_n (Fig. 12.28). Black phosphorus (also P_n) possess graphite-like structure, but the layers are corrugated rather than planar, each P atom being bound to three neighbours.

White phosphorus is unstable and changes very slowly at room temperature to the stable form. It is extremely reactive. Red and black phosphorus are relatively inert. Red phosphorus can be obtained by heating the white form, in the absence of air, for several hours at 540–570K. Red phosphorus is the stable form.

Red phosphorus can be reverted back to white phosphorus by heating, in the absence of air, until it vapourizes and then condensing the vapour. Black phosphorus is made by heating white phosphorus to 473K under high pressure or at 520–650K for 8 days in the presence of mercury as a catalyst and with a seed of black phosphorus. It exists in three crystalline and one amorphous forms. A comparison of the properties of the white and red allotropes of phosphorus is given in Table 12.14. Interconversion of the allotropes can be effected as suggested through Fig. 12.29.

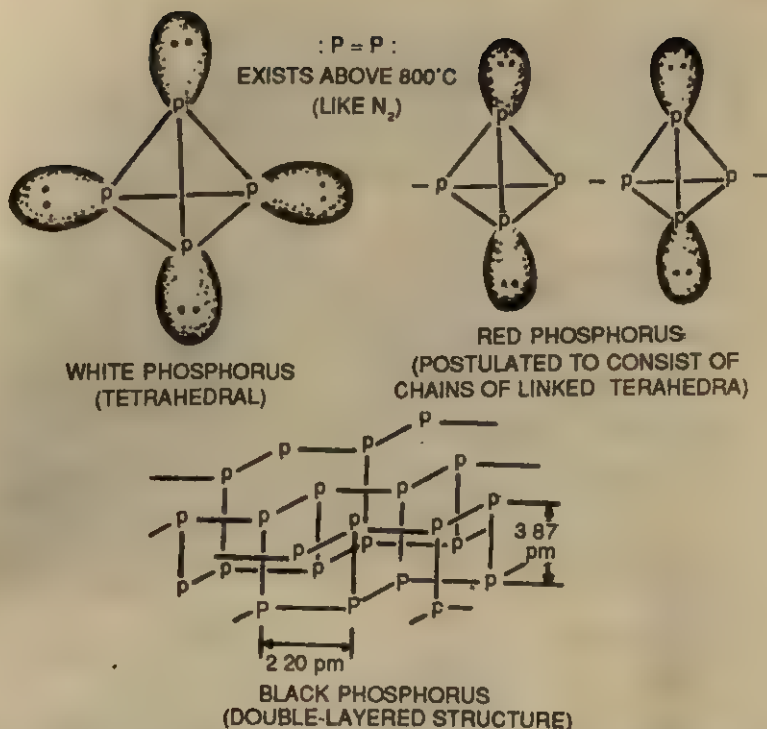


Fig. 12.28 The broad spectrum of the arrangement of atoms in the different allotropic forms of phosphorus.

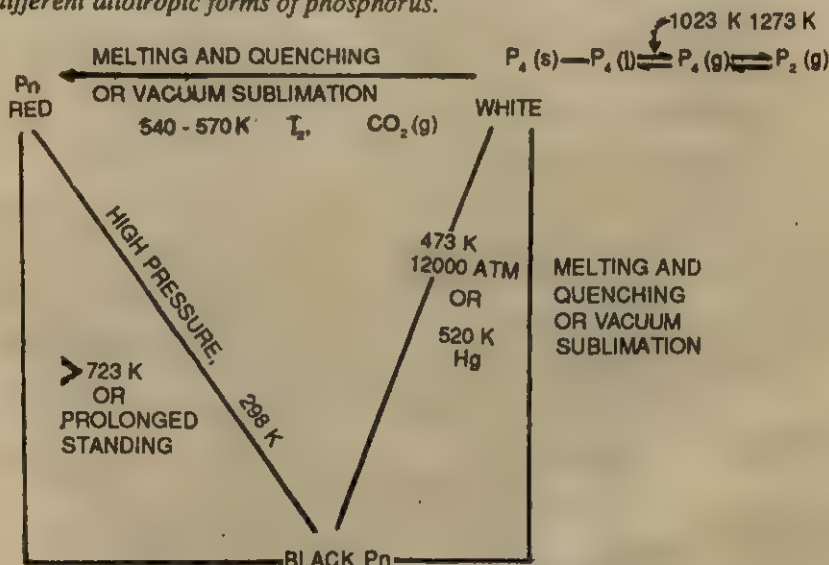


Fig. 12.29 Inter conversion of allotropes of phosphorus.

12.13.3 Isolation of Phosphorus

Phosphorus is usually extracted from rock phosphate, $\text{Ca}_3(\text{PO}_4)_2$, by mixing it with silica and coke and heating it in an electric furnace at 1800K (Fig. 12.30)



In the course of the reaction, silicon (IV) oxide (acidic oxide) displaces the more volatile P_4O_{10} from rock phosphate (P_4O_{10} is acidic) and combines with CaO (basic; one of the constituents of rock phosphate) to form calcium silicate. Phosphorus (V) oxide is then reduced by carbon to elemental phosphorus. As the phosphorus is formed, it vapourizes. The vapours are condensed; white phosphorus is then collected as a liquid under water. On cooling, it solidifies.

TABLE 12.14 Physical and chemical properties of white and red phosphorus

Property	White phosphorus	Red phosphorus
1. State and colour	White waxy solid	Purple-red amorphous powder
2. Density (g/cm^3)	1.8	2.2
3. Smell	Garlic-like	No smell
4. Melting point (K)	317	773-873 (under pressure)
5. Toxicity	Very poisonous	Non-poisonous
6. Solubility	Insoluble in water; Soluble in CS_2 and other solvents	Insoluble in water, CS_2 and other organic solvents
7. Ignition	Ignites at 308K; burns spontaneously in air	Ignites at 530K
8. Phosphorescence	Greenish glow	No phosphorescence
9. Reactivity	Very reactive	Less reactive
10. Storage	Under water	Can be stored easily
11. Reaction with Cl_2	Ignites spontaneously giving PCl_3 and PCl_5	Reacts on heating forming PCl_3 and PCl_5
12. Reaction with alkalis	Produces PH_3 on heating	No reaction

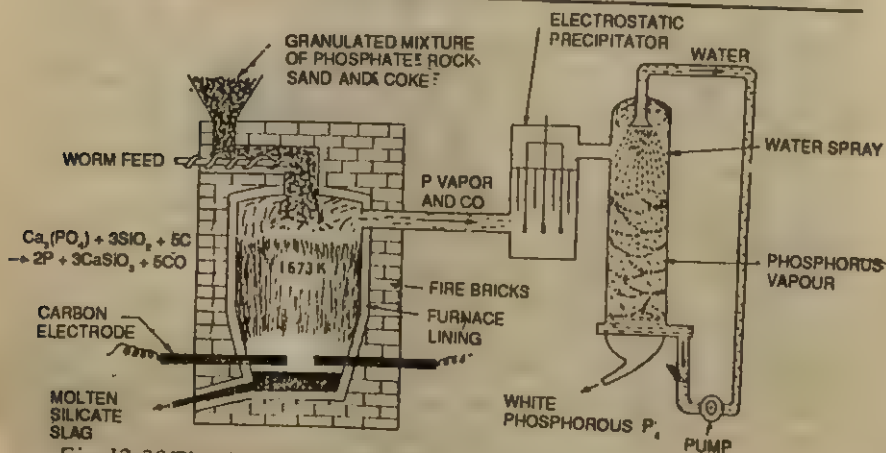
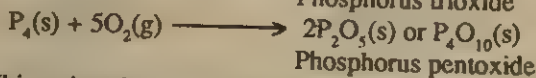
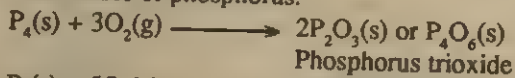


Fig. 12.30 The electrothermal production of phosphorus

12.13.4 Properties of Phosphorus

Many of the physical properties of the various allotropic forms of phosphorus have been listed in Table 12.14. White phosphorus is the most reactive. It decomposes at $\sim 1073\text{K}$ to give P_2 molecules. In contrast to nitrogen, phosphorus is extremely reactive.

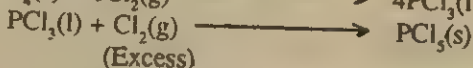
1. **With air (dioxygen)** : Because of its low ignition temperature, it catches fire in dioxygen (or air) producing dense white fumes, consisting of the oxides of phosphorus.



White phosphorus glows in the dark because its vapours are oxidized by atmospheric oxygen with the emission of light.

Red phosphorus burns to give P_4O_{10} , only when heated above 533K .

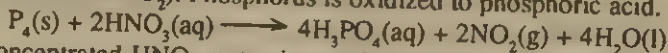
2. **With halogens** : Phosphorus reacts with the halogens exothermally. White phosphorus ignites spontaneously in chlorine to form tri- and pentachlorides.



Red Phosphorus reacts with chlorine at high temperature forming tri and pentachlorides.

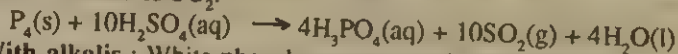
Phosphorus reacts with fluorine, bromine and iodine forming trihalides and pentahalides. Only PI_5 is not known.

3. **With acids** : White phosphorus reacts explosively with conc. HNO_3 (reduced to NO_2). Phosphorus is oxidized to phosphoric acid.



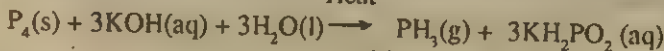
Concentrated HNO_3 reacts vigorously on warming with red phosphorus in the presence of a trace of iodine as catalyst.

Hot concentrated H_2SO_4 yields phosphoric acid with phosphorus and is itself reduced to SO_2 .



4. **With alkalis** : White phosphorus reacts with hot strong aqueous caustic soda (NaOH) or KOH to form phosphine (not dihydrogen).

Heat



Phosphine Potassium hypophosphite

Red phosphorus does not react with alkalis.

Some of the typical reactions of phosphorus are given in Fig. 12.31.

12.13.5 Uses of Phosphorus

Some of the important uses of phosphorus are listed below :

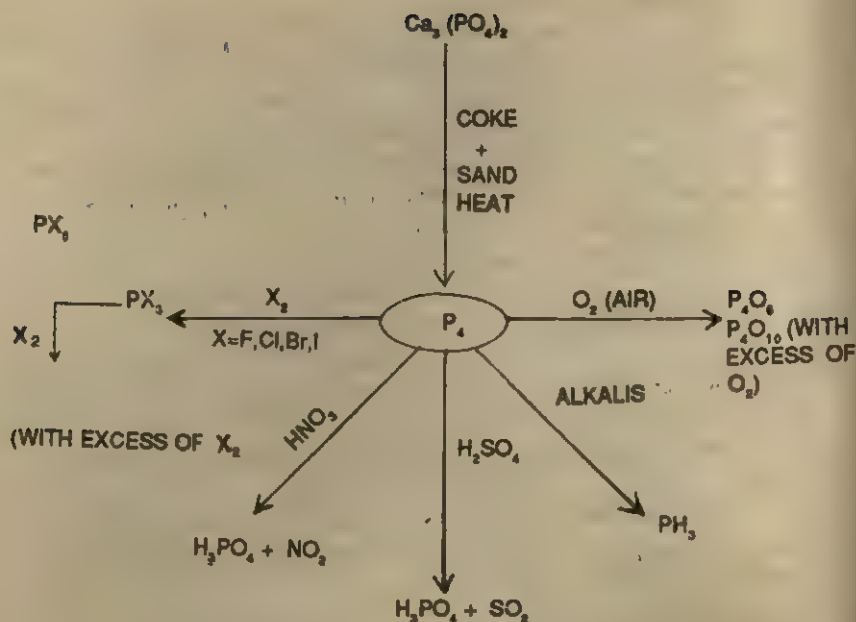


Fig. 12.31 some of the typical reaction of phosphorus.

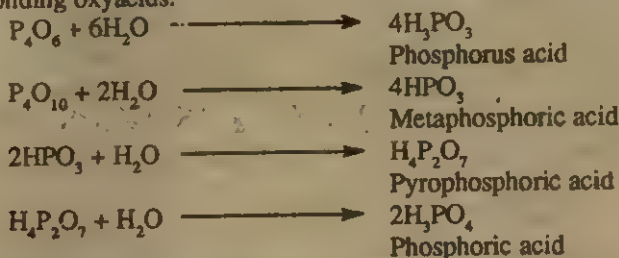
1. Phosphorus is used in the manufacture of phosphoric acid (used in the preparation of phosphatic fertilizers), phosphorus pentoxide (dehydrating agent), sodium metaphosphate (used for softening water), phosphor-bronze, a very hard alloy of copper, tin and phosphorus (being highly resistant to corrosion is used in making electrical gadgets), phosphine (used for producing smoke screen), etc.
2. It is used in making its chlorides and sulphides which are used in the manufacture of insecticides and plasticisers.
3. It is used in the manufacture of certain complex organic phosphates which are constituents of synthetic detergents.
4. Red phosphorus is used in the manufacture of tetra-phosphorus trisulphide P_4S_3 , which is used in making matches.
5. It is used in making rat poisons.
6. As the combustion of white phosphorus produces dense white smoke, phosphorus is used for making incendiary bombs, smoke bombs and fireworks.

12.14 COMPOUNDS OF PHOSPHORUS

12.14.1 Oxides

Oxides corresponding to oxidation states +3 and +5 are the two principal oxides of phosphorus, P_4O_6 and P_4O_{10} , obtained when phosphorus is burnt in air (O_2). The lower oxide is obtained in a limited

supply of air. Both P_4O_6 and P_4O_{10} are the acid anhydrides of H_3PO_3 and H_3PO_4 respectively. Thus, both the oxides on hydrolysis give their corresponding oxyacids.



The structures of these oxides is based on a tetrahedral arrangement of four phosphorus atoms. These phosphorus atoms are linked by six bridging oxygen atoms in the case of P_4O_6 . (Fig. 12.32 a). But in the case of P_4O_{10} , in addition to six bridging oxygen atoms, each phosphorus atom is attached to a fourth oxygen atom (Fig. 12.32 b) which is directed away from the P_4 tetrahedron. The disposition of oxygen atoms around each phosphorus atom is thus tetrahedral.

Phosphorus pentoxide has strong affinity for water; it even removes the elements of water from conc. H_2SO_4 . Thus, it serves as a good dehydrating agent.

12.14.2 Oxyacids

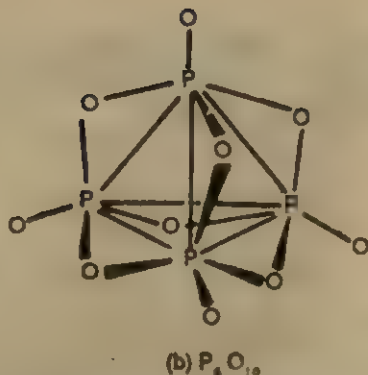
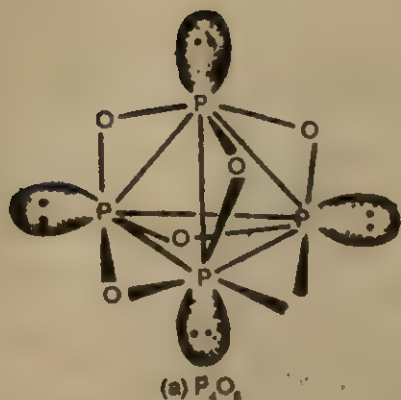
The common oxyacids of phosphorus are listed in Table 12.15.

TABLE 12.15 Oxyacids of phosphorus

Oxidation state	Molecular formula		Name
+1	H_3PO_2		Hypophosphorous acid
+1	H_2PO_3	Ortho- Meta- Pyro-	Phosphorous acid
+3	HPO_3		
+3	$H_4P_2O_5$		
+4	$H_2P_2O_6$		Hypophosphoric acid
+4	H_4PO_4	Ortho- Meta- Pyro-	Phosphoric acid
+5	HPO_4		
+5	$H_4P_2O_7$		

The most highly hydroxylated acid known in a particular oxidation state is the ortho acid. The meta acid is obtained by the loss of one molecule of water from the ortho acid and the pyro acid is the intermediate produced by the action of heat and loss of a water molecule from two molecules of ortho acids. The prefix, 'hypo' generally shows a lower oxygen content than the parent acid. This is all illustrated in Fig. 12.33 for the phosphorus acids.

The oxyacids of phosphorus contain acidic hydrogens bonded to oxygen.



TETRAHEDRON OF OXYGENS
ABOUT EACH PHOSPHORUS

Fig. 12.32 Structures of (a) P_4O_6 and (b) P_4O_{10}

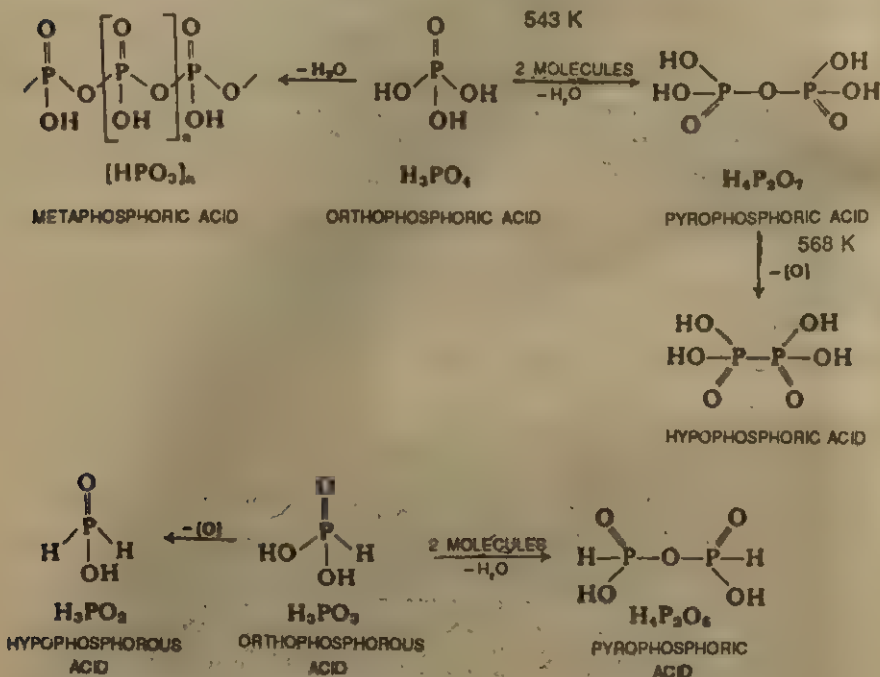
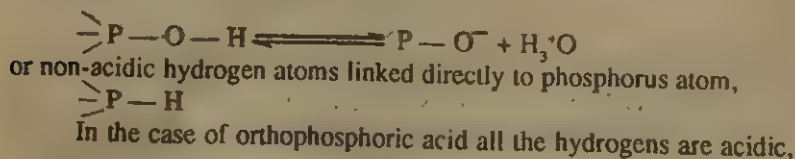


Fig. 12.33 Some oxyacids of phosphorus.



and hence, can be ionized.

Phosphorus has a tendency to form condensed oxyanions, which are obtained when two or more PO_4^{3-} units can join together through the process of sharing of one or two oxygen atoms. This situation parallels to the phenomenon found in silicate structures. In condensed phosphates, as well as in the simple oxyanions, the element is always tetrahedrally co-ordinated (Figs. 12.34 and 12.35). In the oxyanions of phosphorus, $\text{P} - \text{O}$ σ bonds are supplemented by delocalized π bonding.

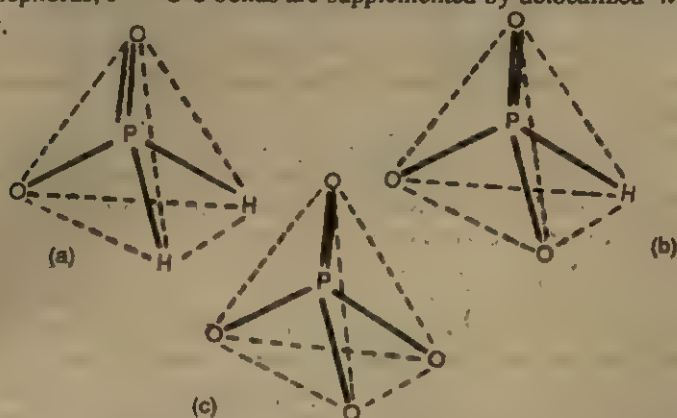


Fig. 12.34 Tetrahedral structure of the ions : (a) hypophosphite, (b) phosphite, and (c) phosphate.

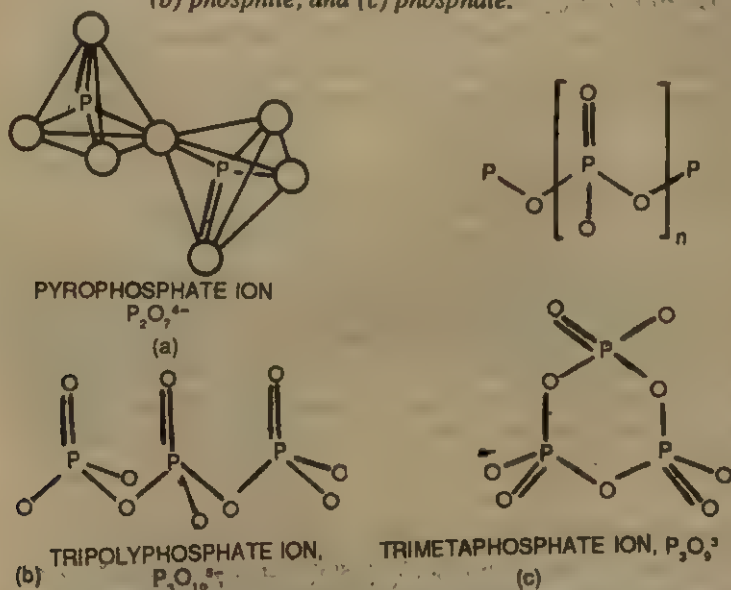


Fig. 12.35 Tetrahedral structure of the ions: (a) pyrophosphate, $(\text{P}_2\text{O}_7)^{4-}$ (b) tripolyphosphate, $(\text{P}_3\text{O}_{10})^{5-}$ and trimetaphosphate $(\text{P}_3\text{O}_6)^{3-}$ (linear and cyclic).

In the discussion of the oxyacids, you have come across, -P-P- and -P-O-P- linkages. Condensed acids containing -P-P- bonds are more slowly hydrolysed than those containing P-O-P bonds. The -P-O-P- linkages are of great biochemical importance. Certain biologically active molecules on which all life depends, e.g., adenosine triphosphate (ATP) contains this linkage. This phosphate ester plays a vital role in life process such as, protein synthesis, genetic coding, photosynthesis, nitrogen fixation and many other metabolic pathways. Hydrolysis of this ester releases the energy required for many biochemical processes. Thus, phosphate groups are called "high energy phosphate".

Orthophosphoric acid is a major industrial chemical. It is manufactured either by treating rock phosphate (or bone ash) with conc. H_2SO_4 or by hydrating phosphorus pentoxide.

The pure acid forms colourless deliquescent crystals that melt at 315.4K. The pure acid is a three dimensional hydrogen bonded structure. It is often sold as an 85% solution in water called 'syrupy phosphoric acid'. The high viscosity of this solution arises from intermolecular hydrogen bonding. It is a relatively weak triprotic (or tribasic) acid and forms three series of salts: sodium hydrogen phosphate, NaH_2PO_4 , (weakly acidic), disodium hydrogen phosphate, Na_2HPO_4 (weakly alkaline) and trisodium phosphate, Na_3PO_4 (strongly alkaline). Most phosphates are insoluble in water.

Uses of Phosphates and Phosphoric Acids

Naturally occurring calcium phosphate and the acid obtained from it are used in the manufacture of fertilizers. Reaction with conc. H_2SO_4 , HNO_3 or phosphoric acid yields the fertilizers, e.g., super phosphate of lime. Sodium hexametaphosphate, 'calgon' is used as a water softener. Phosphoric acid is used in the rust proofing of steel. Pure acid produced from P_4O_{10} is used in the preparation of phosphate salts which are used in food, detergent and pharmaceutical industries. Pure acid is also used in medicine as astringent, antiseptic and stimulant.

12.15 CHEMICAL FERTILIZERS

Increasing population is putting strains on the food resources of this planet. Chemistry plays a very important role in the development of agriculture and in the production of more and better food. Chemical fertilizers or manures are added to the soil to increase its fertility.

Three elements, i.e., nitrogen (for leaf growth), phosphorus (for root growth) and potassium (for flowering) are the primary or macro-nutrients. These are used up by plants and the soil suffers a deficiency of compounds of these elements in soil. Apart from these, iron, calcium, magnesium and sulphur, called secondary nutrients, are also required in small quantities. Later it was discovered that elements like, Co, Zn, Mo, Cu, Mn, Cl and B play key roles in plant nutrition. Their deficiency in soil is less common.

A manure is a natural substance obtained by the decomposition of animal excreta or plant residues. A chemical fertilizer is an artificially produced salt or some other chemical substance (organic or inorganic) containing the necessary plant nutrients. The elements are present in such forms that plant can readily make use of them.

Some of the common fertilizers are listed below :

1. **Nitrogenous fertilizers** : Ammonium sulphate, ammonium nitrate, sodium nitrate, urea, calcium cyanamide, calcium ammonium nitrate (CAN)
2. **Phosphatic fertilizers** : Superphosphate of lime or triple superphosphate
3. **Potassium or potash fertilizers** : Potassium chloride, potassium nitrate

Fertilizers which contain only one primary nutrients (i.e., N, P or K) are called single fertilizers. Fertilizers composed of more than one primary nutrients are known as 'mixed fertilizers'. According to the contents, they are classified as NK, NP, PK, or NPK type. For example,

- (i) Potassium nitrate, KNO_3 -A fertilizer of NK type
- (ii) Ammonium dihydrogen phosphate, $(\text{NH}_4)\text{H}_2\text{PO}_4$ -A fertilizer of NP type (Amphophos)

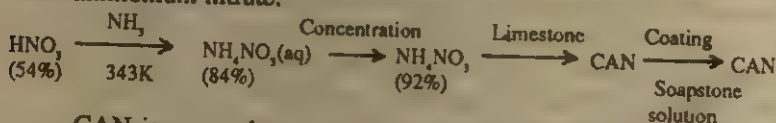
NPK type fertilizers are called complete fertilizers. They supply all the primary nutrients. Fertilizers are marketed with special trade names such as, "Sriram Urea", "Kissan Urea", "Kissan Khad", etc.

Nitrogenous Fertilizers

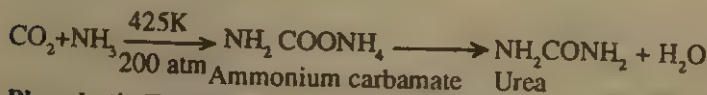
1. **Ammonium sulphate** : In the Sindri fertilizer factory (Bihar) ammonium sulphate is manufactured by a method called gypsum process. In this process ammonia water is conducted into a tank containing pulverized gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) suspended in water. At the same time CO_2 is bubbled through the mixture under high pressure. Ammonium carbonate is first formed which, in turn, reacts with calcium

$$2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{CaSO}_4(\text{l}) \rightarrow (\text{NH}_4)_2\text{SO}_4(\text{aq}) + \text{CaCO}_3(\text{s})$$

2. **Calcium ammonium nitrate (CAN) :** Ammonia is obtained by Haber's process. Ammonia is converted into nitric acid. More of ammonia is allowed to react with nitric acid to produce ammonium nitrate. Now powdered limestone is mixed up with NH_4NO_3 to get calcium ammonium nitrate.



3. Urea a well known nitrogenous fertilizer has a much higher percentage of available nitrogen. It is manufactured by the reaction of CO_2 with NH_3 at 425K



Superphosphate of lime (calcium superphosphate) is obtained on a large scale by the action of conc. H_2SO_4 on insoluble rock phosphate

$$\underset{\text{(Insoluble)}}{\text{Ca}_3(\text{PO}_4)_2} + \text{H}_2\text{SO}_4 + 5\text{H}_2\text{O} \longrightarrow \underset{\text{(Soluble)}}{\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}} + 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$$

It contains 18% P_2O_5 and its active ingredient is monocalcium phosphate which is water soluble. Thus, it provides its phosphate in a water soluble form which is readily assimilated by plants.

To increase the amount of available phosphorus in the fertilizer, double and triple superphosphates are used. These are more effective than simple superphosphates as their phosphorus content is higher because of the absence of calcium sulphate. Triple superphosphate is prepared by treating a weighed amount of rock phosphate with 54% H_3PO_4 in mixers.


$$\text{Ca}_3(\text{PO}_4)_2 + 7\text{NH}_3 + \text{O}_4 \longrightarrow 3\text{Ca}(\text{H}_2\text{PO}_4)_2$$

The soil is usually alkaline in nature which converts the soluble superphosphate into insoluble salts.

Potash Fertilizers

Soluble potassium salts are present in soil as a result of weathering of rocks. For some crops additional quantities of KCl , K_2SO_4 or KNO_3 are helpful.

SELF ASSESSMENT QUESTIONS

Multiple choice Questions

12.1

Put a tick (✓) mark against the correct answer :

- (i) The molecule having one unpaired electron is (IIT 1985)
(a) NO (b) CO (c) CN^- (d) D_2
- (ii) A gas that cannot be collected over water is
(a) O_2 (b) N_2 (c) NH_3 (d) H_2
- (iii) A compound that is a Lewis base is
(a) NH_3 (b) HNO_3 (c) O_2 (d) BeCl_2
- (iv) Hydrogen gas will not reduce (IIT 1985)
(a) heated cupric oxide (b) heated ferric oxide (c) heated stannic oxide (d) heated aluminium oxide.
- (v) Brown ring test is employed for the detection of
(a) NO_3^- (b) NO_2^- (c) SO_4^{2-} (d) CO_3^{2-}
- (vi) The bonds present in N_2O_5 are (IIT 1985)
(a) only ionic (b) covalent and coordinate (c) only covalent (d) covalent and ionic
- (vii) The lightning bolts in the atmosphere cause the formation of :
(a) NO (b) NH_3 (c) NH_4OH (d) NH_2OH (IIT 1986)
- (viii) Which of the following oxides does not produce acid on reacting with water ?
(a) P_2O_5 (b) NO_2 (c) CO_2 (d) Na_2O
- (ix) Which of the following species is nothing to do with photochemical smog?
(a) CO_2 (b) NO_3 (c) NO (d) O_3
- (x) Which of the followings is not a primary nutrient for the soil ?
(a) N (b) P (c) K (d) S
- (xi) Which of the following elements form electron deficient halides ?
(a) B , (b) N (c) Si (d) C
- (xii) Which of the following type of compounds does not involve tetrahedral geometry around the central atom ?
(a) silicates (b) oxyacids of phosphorus (c) borates (d) none
- (xiii) Which of the following substances contains phosphorus ?
(a) calgon (b) carborundum (c) kermite (d) clay
- (xiv) The brown ring complex compound is formulated as $(\text{Fe}(\text{H}_2\text{O})_6\text{NO}^+)\text{SO}_4^-$. The oxidation state of iron is (IIT 1987)
(a) 1 (b) 2 (c) 3 (d) 4
- (xv) Which of the following oxides of nitrogen is a coloured gas ?
(a) N_2O (b) NO (c) N_2O_4 (d) NO_2 (IIT 1987)
- (xvi) Which of the following elements is expected to have the most non-metallic character ?
(a) P (b) S (c) O (d) F

12.2 Indicate which of the following statements is true or false :

- (i) Metals form basic oxides, whereas non-metals form acidic oxides.
- (ii) Hydrogen exhibits properties of a metal as well as of a non-metal.
- (iii) Nitric acid reacts with most of the metals giving similar type of products.
- (iv) NH_3 gas is collected by displacement of air in a inverted bottle.
- (v) Aqua regia is a mixture of hydrochloric acid and nitric acid.

- (vi) Pure nitric acid does not show acidic properties.
- (vii) Dinitrogen is produced by heating ammonium nitrate.
- (viii) Nitrogen dioxide dissolves in rain water to form nitric acid and nitrous acid.
- (ix) Photochemical smog is caused by carbon dioxide.
- (x) Nitrogen, phosphorus and potassium are the primary nutrients for the soil which help in increasing the crop production.
- (xi) The first element in a group behaves differently from the other members of the group.
- (xii) Triphosphates and trimetaphosphates have the same molecular formula.
- (xiii) Carbon dioxide is a gas and whereas silicon dioxide is a high melting solid.
- (xiv) Carborundum is an allotropic form of carbon.
- (xv) Boric acid has a layer structure which is based upon its structural unit BO_2 .
- (xvi) The -P-O-P- linkage associated with ATP is vital for life processes.
- (xvii) Red phosphorus is more reactive than white phosphorus.
- (xviii) Silicone polymers contain silicon in the catenated form.
- (xix) Glass is a man made silicate.
- (xx) The various allotropic forms of phosphorus are temperature dependent.

12.3 Fill in the blanks :

- (i) Hydrogen gas is liberated by the action of aluminium with concentrated solution of (IIT 1987)
- (ii) Water gas is mixture of
- (iii) An oxide which reacts with both acids and alkalis is called
- (iv) Assimilation of atmospheric dinitrogen by plants and animals is called
- (v) Nitric acid is manufactured by the catalytic oxidation of
- (vi) Thermal decomposition of gives boron.
- (vii) is the simplest hydride of boron.
- (viii) Boron dissolves in water to give solution.
- (ix) Boric acid differs from other protonic acids. It acts as a by accepting
- (x) Silicon dissolves in hot aqueous alkali to liberate
- (xi) Asbestos is one of the types of
- (xii) The basic structural unit in silicates and silica is
- (xiii) The constituents of soda glass are
- (xiv) Hydroxyapatite is the mineral of
- (xv) Pyrophosphoric acid is a product of orthophosphoric acids.
- (xvi) Superphosphate of lime is represented by the molecular formula

12.4 Match the descriptions under column B against the terms/statements given under column A.

Column A	Column B
1. Non-metals	(a) Haber's process
2. Metals	(b) a fertilizer
3. Hydrogen	(c) replace dihydrogen from acids
4. Ammonia	(d) do not replace dihydrogen from acids
5. Ostwald's process	(e) oxidation state, -3
6. Acid rain	(f) a process for producing dihydrogen gas
7. Bosch's process	(g) an ore of boron
8. Calgon	(h) NO_2
9. Colemanite	(i) a silicate
10. Pyroxene	(j) a condensed phosphate
11. Urea	(k) a method of producing nitric acid
12. CO_2	(l) green house effect

SHORT ANSWER QUESTIONS

- 12.5** (i) Write down the resonance structures of nitrous oxide.

(IIT 1985)

- (ii) What happens when aqueous ammonia is added dropwise to a solution of copper sulphate until it is in excess. (IIT 1988)
- (iii) Gold is dissolved in aqua regia. Give the balanced equation. (IIT 1987)
- (iv) Name the gases produced in the following reactions :
- A mixture of slaked lime and ammonium chloride is heated.
 - A mixture of sodium nitrite and ammonium chloride is heated.
 - Zinc is treated with dilute sulphuric acid.
 - Calcium carbonate is treated with dilute HCl.
 - Atmospheric O_2 and N_2 combine in the presence of sunlight.
- (v) Write equations for the following reactions :
- Reaction of ammonia with chlorine.
 - Reaction of ammonia with dioxygen.
 - Reaction of dihydrogen on ferric oxide.
 - Reaction of nitric acid on copper.
 - Reaction of aqueous sodium hydroxide on boron.
 - Reaction of hot aqueous alkali on silicon
- (vi) State the difference between salt-like and covalent hydrides.
- (vii) Why does elemental dihydrogen react with other substances only slowly at room temperature.
- (viii) How would you prepare dihydrogen
- from water, (2) from a substance other than water, (3) metal and (4) heavy hydrogen ?
- (ix) Choose the acidic and basic anhydride of the following compounds. Give their reactions with water; Na_2O , P_2O_5 , SO_2 , Al_2O_3 .
- (x) (a) Nitric acid lying in a bottle appears yellow. Comment ?
(b) In the laboratory preparation of HNO_3 , gentle heating is advised. Comment.

12.6

- What are condensed phosphates ?
- Name two important minerals of boron with their formulae.
- What are electron deficient compounds ?
- What happens when boron is treated with an acid ?
 - Name the products which are obtained when boric acid is heated.
- Silicon does not form an analogue of graphite. Comment.
- How does silicon show a higher covalency than carbon ?

TERMINAL QUESTIONS

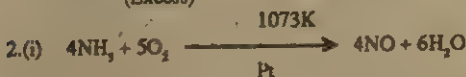
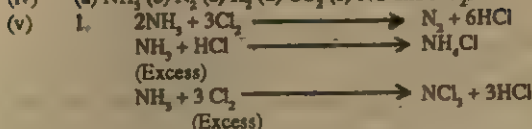
- 12.1 (a) How do the physical properties of metals differ from those of non-metals?
(b) Compare the metals and non-metals with respect to (i) hydrolysis of oxides, (ii) reaction with acids, (iii) combination with dihydrogen, and (iv) nature of chlorides.
- 12.2 (i) Discuss the position of hydrogen in the periodic table.
(ii) Name the various isotopes of hydrogen.
(iii) State the uses of dihydrogen and heavy water.
- 12.3 (i) Justify the diagonal relationship between boron and silicon.
(ii) What do you understand by the term allotropy ?
(iii) State the uses of phosphorus and its compounds.
- 12.4 Comment on each of the following :
- NH_3 gas is collected by displacement of air in an inverted bottle.
 - Dinitrogen cannot be dried over anhydrous $CaCl_2$ or P_2O_5 .
 - Red phosphorus does not catch fire spontaneously.
 - $AgCl$ dissolves in aqueous ammonia.
 - Aqueous nitric acid is a strong acid.
 - Traces of nitric acid are found in rain water after lightning.
- 12.5 Give an evidence that can justify that the bond between the proton and an ammo-

- nia molecule is stronger than that between the proton and water.
- 12.6 (a) Outline the chemistry involved in the production of nitric acid from ammonia.
 (b) List the possible reduction products of nitric acid. What factors determine which product will be formed when nitric acid is reduced?
- 12.7 (a) Account for almost complete absence of free dihydrogen in nature.
 (b) What happens to the electrical energy that is used in the electrolysis of water?
 (c) Name three metals that will displace dihydrogen from (i) cold water, (ii) steam and (iii) acids. Give the balanced equations for each.
- 12.8 (a) Explain the following:
 (i) The boiling point of NH_3 is higher than PH_3 and AsH_3 .
 (ii) Nitrogen does not form any pentachloride.
 (b) What is the structure of nitric acid in all the three states: gas, liquid and solid?
 (c) How does the aqueous solution of HNO_3 differ from anhydrous HNO_3 . Illustrate your answer.
- 12.9 What are boron hydrides? Name the simplest hydride and discuss its structure. Does the structure has any relation to that of elemental boron?
- 12.10 Describe the chemical reactions for each silicon and boron which could support their non-metallic character.
- 12.11 Comment on the existence of the great variety of silicates in terms of the manner of linking of SiO_4 tetrahedra.
- 12.12 What is glass? Give the various types of glasses? Describe briefly the method of its preparation.
- 12.13 (a) Calculate the oxidation state of phosphorus in each of the followings: P_4O_{10} , H_3PO_4 , $\text{H}_2\text{P}_2\text{O}_7$, PH_3 and H_3PO_3 .
 (b) Compare the properties of white and red phosphorus.
- 12.14 Give the chemical properties of phosphorus and nitrogen which could illustrate the difference between them and their corresponding oxyacids (HNO_3 and H_3PO_4) and hydrides (NH_3 and PH_3).
- 12.15 What are condensed phosphates? Support your answer with examples.
- 12.16 (a) Why does phosphorus acid form only two types of salts although its molecule contains three hydrogen atoms?
 (b) Comment on the nomenclature of the oxyacids of phosphorus.
 (c) How do you prepare orthophosphoric acid?
- 12.17 (a) What are artificial fertilizers? How do they differ from natural fertilizers?
 (b) What are primary and secondary nutrients?
 (c) Give the outlines for the preparation of CAN.

ANSWERS TO SELF ASSESSMENT QUESTIONS

- 12.1 (i) a, (ii) c, (iii) a, (iv) d, (v) a, (vi) b, (vii) a, (viii) d, (ix) a, (x) d, (xi) a, (xii) c, (xiii) a, (xiv) a, (xv) d, (xvi) d.
- 12.2 (i) T, (ii) T, (iii) F, (iv) T, (v) T, (vi) F, (vii) T, (viii) T, (ix) F, (x) T, (xi) T, (xii) F, (xiii) T, (xiv) F, (xv) F, (xvi) T, (xvii) F, (xviii) F, (xix) T, (xx) T.
- 12.3 (i) Sodium hydroxide (ii) CO and H_2 (iii) amphoteric oxide (iv) nitrogen fixation (v) ammonia (vi) boron hydrides (vii) diborane (viii) alkaline (ix) Lewis acid, hydroxyl ion. (x) hydrogen (xi) silicates (xii) $(\text{SiO}_4)^{4-}$ (xiii) Na_2SiO_3 , CaSiO_3 , 4SiO_2 (xiv) phosphorus (xv) Condensed, two units, (xvi) $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$
- 12.4 1 (d) 2 (c) 3 (a) 4 (c) 5 (k) 6 (h) 7 (f) 8 (j) 9 (g) 10 (i) 11 (b) 12 (l)
- 12.5 (i) $\text{N}^{3-} = \text{N}^{+} = 0 \longrightarrow \text{N} \equiv \text{N}^{+} - \text{O}^{-}$
 (ii) To start with a bluish white ppt. of $\text{Cu}(\text{OH})_2$ is obtained which dissolves in excess of ammonia and gives a deep blue coloured complex, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$
 (iii) $\text{Au} + 3\text{HNO}_3 + 4\text{HCl} \longrightarrow \text{HAuCl}_4 + 3\text{NO}_2 + 3\text{H}_2\text{O}$

(iv) (a) NH_3 (b) N_2 (c) H_2 (d) CO_2 (e) NO and NO_2

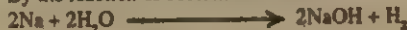


(vi) (i) Salt like hydrides are ionic in nature. They have properties that are characteristic of an ionic compound. They are formed by the alkali and the alkaline earth metals except Be and Mg.

(ii) Covalent hydrides are formed by p-block elements. They are usually gases or volatile liquids under normal conditions. The bonds are not significantly polar. Bonds are generally formed by electron sharing.

(vii) This is because of its very high bond dissociation energy.

(viii) 1. By the reaction of sodium over water



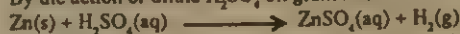
Also by the reaction of water over coke.

1270K

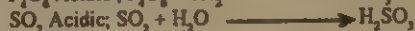
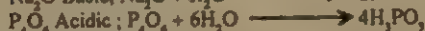


2. As a by-product in the electrolysis of brine solution (conc. NaCl solution) for the manufacture of NaOH .

3. By the action of dilute H_2SO_4 on granulated zinc metal.



4. By the electrolysis of heavy water which is obtained by the prolonged electrolysis of acidified water.



Al_2O_3 Amphoteric; It reacts both with acids and alkalis.

(x) (a) Conc. HNO_3 is yellow due to dissolved NO_2 produced by its photochemical decomposition.

(b) Nitric acid is often decomposed by heat of reaction and the NO_2 formed dissolves in acid, making it yellow.

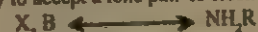


12.6 1. When two or more PO_4 units join together, a product called condensed phosphate is obtained.

2. (i) Borax, $\text{Na}_2\text{B}_4\text{O}_7(\text{OH})_4 \cdot 8\text{H}_2\text{O}$

(ii) Colemanite $\text{Ca}_2[\text{B}_3\text{O}_6(\text{OH})_2]_2 \cdot 2\text{H}_2\text{O}$

3. A compound in which the number of electrons around the central atom is less than eight, e.g., BX_3 ($\text{X} = \text{Cl}, \text{F}, \text{Br}, \text{I}$). Such a compound has a tendency to accept a lone pair of electrons.



4. (a) Borax on treating with an acid gives boric acid.





5. The graphite structure is not adopted by the element because of the inability of the atoms to form $p\pi - p\pi$ with each other.
6. Silicon utilizes its 3d orbitals which are vacant for bond formation, e.g., SiF_6^{2-} .

UNIT 13

Chemistry of Non-Metals - II

(Oxygen, Sulphur, Halogens and the Noble Gases)

Nothing is created out of nothing, By necessity were foreordained all things that were and are to be.

..... Democritus

UNIT PREVIEW

- 13.1 Introduction
- 13.2 Oxygen and sulphur - general characteristics
- 13.3 Oxygen
- 13.4 Simple oxides
- 13.5 Ozone
- 13.6 Water and hydrogen peroxide
- 13.7 Sulphur
- 13.8 Compounds of sulphur : H_2S , oxides of sulphur - SO_2 and SO_3 , sulphuric acid and sodium thiosulphate
- 13.9 Halogens
- 13.10 Compounds of halogens : interhalogen compounds, hydrogen halides
- 13.11 Noble gases
- Self assessment questions
- Terminal questions
- Answers to self assessment questions

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Differentiate between metals and non-metals with reference to their physical characteristics.
2. Classify the oxides - acidic, basic or neutral - of metals and non-metals on the basis of their reaction with water.
3. Characterize the non-metals on the basis of their chemical properties, e.g., reaction with acids, etc.
4. Understand the concept of allotropy seen among various non-metals.
5. Give reasons for the inert nature of noble gases and extremely reactive behaviour of halogens lying close to them.
6. Give the principal sources and common methods of preparation of the noble gases, the halogens and the chalcogens.
7. Compare the manner in which the individual members of each of the groups of elements differ from the another.
8. Describe the general reactivity of the elements of each group and the behaviour of their compounds.
9. Describe the various aspects of water including ice, and hydrogen peroxide and ~~hydrogen~~
10. Explain the working principle of Kipp's apparatus employed for the preparation of H_2S gas.
11. Give a few reactions of H_2S suggesting its use for qualitative inorganic analysis.
12. Explain the principle involved in the contact process for the manufacture of sulphuric acid.
13. Describe the nature of sulphuric acid on the basis of its reactions.
14. Give evidences in the support of non-metallic behaviour of the elements included in this unit.

13.1 INTRODUCTION

In the Unit 12, you have learnt the chemistry of hydrogen, boron, silicon, nitrogen and phosphorus. Following these elements are a few groups which include elements of diverse nature, *e.g.* oxygen and sulphur (group 16); halogens (group 17); noble gases (group 18). All these elements constitute p-block elements, about the general behaviour of which we have already discussed in Unit 12.

Group 16 elements are called chalcogens. This name was derived from the Greek name for copper, since most of copper ores contain members of the group. Although, there are many similarities among the members of the family, more irregularities exist than among the halogens, and this is especially true for oxygen. Halogens are the most reactive of the non-metals in their respective rows of the periodic table and, except for the noble gases, have the highest electronegativity in each row.

Noble gases provide a bridge between the strongly electronegative halogens (group 17) and the strongly electropositive alkali metals (group 1). You remember that Mendeleev had not provided any place for this group of elements. The chemical inertness of these elements led the earlier workers to suggest that they be included in the Mendeleev's periodic table by an expansion of that table to include a group '0' (now group 18) after halogens. Their stability has played an important role in the development of periodic table and the concept of the chemical bond.

Alongwith the chemistry of non-metals listed in this unit, we shall also study the manufacture and uses of the some industrially important chemicals, such as, hydrogen peroxide, sulphuric acid, hydrohalic acids, etc.

13.2 OXYGEN AND SULPHUR—GENERAL CHARACTERISTICS

In this unit, you will study the chemistry of oxygen and sulphur which belong to group 16 of the periodic table. These two elements and the other members of the group show less electronegative character than the halogens. Similar to the other groups, metallic character increases with increasing atomic masses. Oxygen and sulphur are non-metallic. The properties of oxygen usually differ significantly from sulphur and the other members of the group because of the absence of low energy d orbitals.

The valence shell electron structure for group 16 elements is ns^2np^4 and all show tendency to gain or share two additional electrons in many of their compounds. All the family members form compounds of the type H_2E ($E = O, S, Se, Te$) wherein the oxidation state of E is -2. As you have seen in Unit 12, oxygen can bond to a maximum of four atoms but sulphur and other members of the family can bond covalently to as many as six other atoms, *e.g.*, SF_6 . The availability of vacant d orbitals is responsible for this phenomenon. The positive oxidation states do not occur for oxygen because of its high electronegativity. Completion of the octet of electrons in the valence shell of oxygen is achieved by (i) forming the dinegative oxide ion O^{2-} (solid state only) (ii) exercising a covalency of two single bonds, *e.g.*,

H—O—H or (iii) forming a double bond with other atoms, *e.g.*, O = C = O (also S=C=S). Sulphur and other elements also form M^{2-} ions but only with the most electropositive elements, *e.g.*, Na_2S . Elements other than oxygen also form compounds of the type H—O—H, but with decreasing stability down the group. Oxygen can also complete its octet by gaining one electron and then by forming one bond, *e.g.* OH^- . Other elements also form such ions, *e.g.*, SH^- , SeH^- , TeH^- but decrease in stability. Oxygen is smaller and more electronegative than sulphur and the other elements. As a result, oxygen compounds are more ionic than that of sulphur. Its electronegative nature is also responsible for the presence of hydrogen bonding in water, which is almost completely absent in hydrogen sulphide.

The presence of hydrogen bonding changes the properties of the compounds significantly (Unit 6). Table 13.1 gives the comparative studies of the properties of the members of oxygen family.

TABLE 13.1 Properties of the oxygen group elements

Property	O	S	Se	Te
Atomic number	8	16	34	52
Electron structure (Valence shell)	$2s^2 2p^4$	$3s^2 3p^4$	$3d^{10} 4s^2 4p^4$	$4d^{10} 5s^2 5p^4$
Covalent radius				
double bond	62	94	107	127
single bond	66	104	117	137
Ionic radius, M^{2-} (pm)	140	184	198	221
Electronegativity	3.5	2.45	2.5	2.0
Electron affinity, M^{2-} , (kJ mol ⁻¹), M^{-1}	-700 141	-330 196	-406 —	— —
Ionization energy, 1st (kJ mol ⁻¹)	1314	1000	941	869
Density (g/cm ³)	1.14	2.07	4.79	6.25
Melting point (K)	55	392	490	723
Boiling point (K)	90	717.6	957.8	1663
Oxidation states	-2	-2, 2, 4, 6	-2, 2, 4, 6	-2, 2, 4, 6
Abundance (ppm)	466000	520	0.09	0.002
Bond energy, M-M (kJ mol ⁻¹)	395	214	184.8	138.6

13.3 OXYGEN

Scheele discovered oxygen some time during the period 1771-3 but did not not disclose about his discovery until 1777. In the meantime, Joseph Priestley prepared dioxygen on 1st August, 1774 by heating mercuric oxide with sun rays. He also produced dioxygen by heating red lead. Priestley related his discovery to Lavoisier, who considered its significance in relation to his own work - combustion, respiration and calcination of metals.

Lavoisier recognized the gas as an element, finally naming it oxygen (Greek, oxys means sour or acid, genon means to form) as the products of combustion appeared to him to be acidic.

Oxygen is the most indispensable of all the elements for almost all forms of life. Living organisms derive energy for their vital functions through oxidation of substances by oxygen in their body or through respiration.

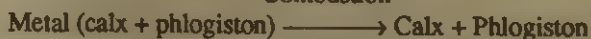
Oxygen is a typical non-metal. It has 6 electrons in the valence shell. Oxygen is a diatomic molecule. It exists in the form of discrete molecules. Two oxygen atoms are joined together by double bonds (Unit 6).

Dioxygen is unique among diatomic molecules. It contains an even number of electrons (16) but two of them are found to be unpaired (spin free). Dioxygen is, therefore, paramagnetic (Unit-6).

13.3.1 Phlogiston Theory and The Discovery of Oxygen

In 18th century, many chemists believed that any thing that burned contained a substance called phlogiston (from the Greek "word to set on fire"). Phlogiston might be considered to be fire itself. Later combustion was considered simply the release of phlogiston from the combustible substance into the air.

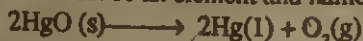
Combustion



Its existence could be established by burning a substance and noting that in the process it has lost its weight. Priestley had prepared dioxygen by heating mercuric oxide with sun rays. The gas was found to help a candle to burn more brightly than in air; it was named 'dephlogisticated air'. Lavoisier carried out a series of experiments. His careful quantitative experiment on combustion led him to realize that metals like zinc, mercury and non-metals like sulphur and phosphorus gain weight on burning. Accordingly he gave a new hypothesis as an alternate to phlogiston: "Combustion is the combination of the combustible substance with dioxygen of the air rather than a decomposition of the combustible substance into phlogiston and calx." Thus, the reduction of an oxide by charcoal (carbon) involved the transfer of oxygen from the oxide to the carbon to form oxides of carbon leaving the 'deoxygenated' or reduced metal.



Lavoisier also subjected red specks of mercury to thermal decomposition. As a result, he obtained a gas which could support combustion better than air and a liquid metal, mercury. Since this gas could not be decomposed further, he realized that it must be an element and named it oxygen.

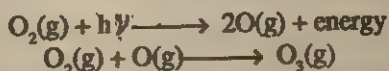


13.3.2 Occurrence

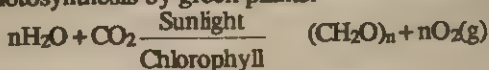
Oxygen occurs in the native state in the atmosphere as diatomic molecules, $\text{O}_2\text{(g)}$ forming about one fifth of atmosphere by mass. Oxygen comprises nearly 50% of the mass of the earth's atmosphere and crust. It occurs in water (89% of the mass) over 70% of the earth's surface including

oxides and oxyanions in the crust (47% of the mass). Quartz and sand are the important oxides. Examples of compounds in which oxygen is present in the oxyanions are nitrate, NO_3^- ; carbonate, CO_3^{2-} ; Sulphate, SO_4^{2-} ; orthophosphate, PO_4^{3-} ; and silicates SiO_3^{2-} .

Atmospheric oxygen contains the three isotopes of oxygen: $^{16}_8\text{O}$, $^{17}_8\text{O}$ and $^{18}_8\text{O}$. In the upper atmosphere, a small amount of atomic oxygen is formed due to the action of ultraviolet light from the sun and the cosmic rays causing dissociation. Atomic oxygen combines with dioxygen to form ozone.



Almost all of dioxygen present in the atmosphere is believed to be the product of photosynthesis by green plants.

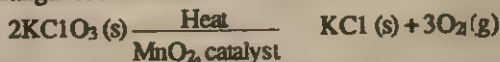


13.3.3 Allotropy in Oxygen

Oxygen has two allotropes, *i.e.*, dioxygen (O_2) and ozone (O_3). Dioxygen is the usual and most abundant form of oxygen. It has a special significance for life on earth. Ozone is mainly present in the upper part of the atmosphere. It is formed by the action of ultraviolet rays on dioxygen. It exists as triatomic molecules.

13.3.4 Preparation of Dioxygen

Dioxygen is prepared in the laboratory by heating a mixture of potassium chlorate and manganese dioxide in the ratio of 4 : 1.



The thermal decomposition of KClO_3 takes place at high temperature, 670-720K. In the presence of manganese dioxide, KClO_3 decomposes at a comparatively low temperature. It is collected in gas jars by the downward displacement of water (Fig. 13.1).

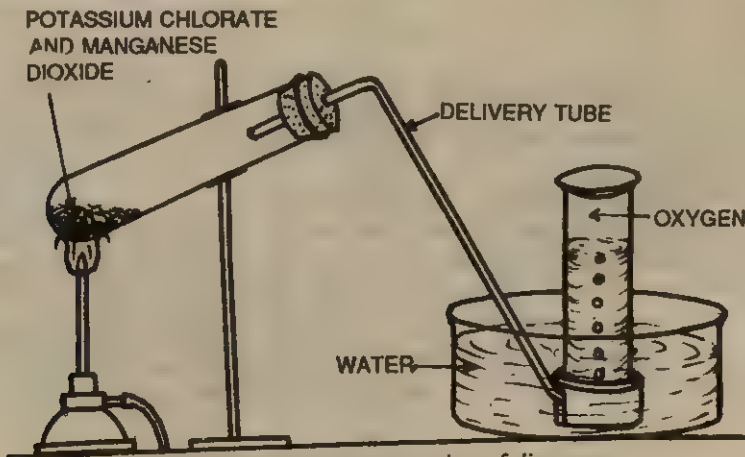


Fig. 13.1 Laboratory preparation of dioxygen

Other oxygen rich compounds like KMnO_4 , Na_2O_2 , etc. can also be employed for the preparation of dioxygen. Dioxygen is obtained commercially by liquefaction of air and subsequent fractional distillation of the liquid to separate O_2 from N_2 . Very pure dioxygen is produced by electrolysis of water.

The methods by which dioxygen can be produced in the laboratory and on a industrial scale are summarized in Fig. 13.2.

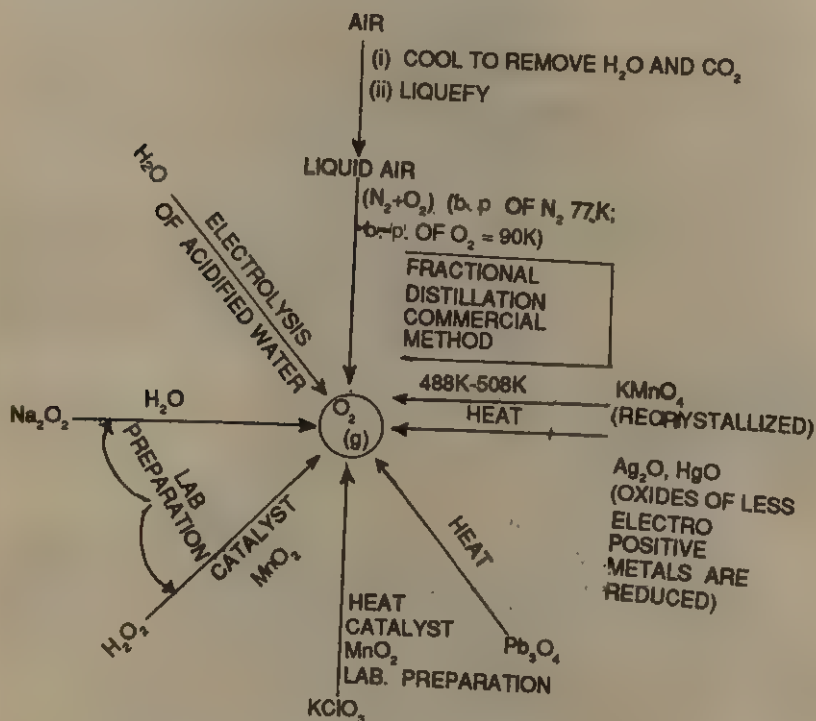


Fig. 13.2 Flow chart diagram showing the various methods of preparing dioxygen.

13.3.5 Properties and Reactions of Dioxygen

Dioxygen is a colourless and odourless gas. It is slightly heavier than air. It is slightly soluble in water (4%). It is neutral toward litmus. It liquefies at 90K to a pale blue liquid and freezes at 54K to a blue solid.

Dioxygen is soluble in water because of hydrogen bonding present between oxygen and H_2O molecules. This small amount of dissolved dioxygen is responsible for sustaining marine and aquatic life and for

destroying organic wastes present in water bodies.

It does not burn but supports combustion. Dioxygen is very active and combines with many other elements both metallic and non-metallic forming binary compounds known as oxides. The reaction between metals and dioxygen is slow because of the high bond dissociation energy of O_2 (> than that of H_2). Hence, the reaction requires strong heating or initiation by external heating.

Most of its reactions with metals and non-metals are highly exothermic. This liberated heat is sufficient enough to take the reaction to completion. Dioxygen combines with a large number of compounds.

On passing electric discharge through purified dioxygen gas diluted with argon atomic oxygen is produced.

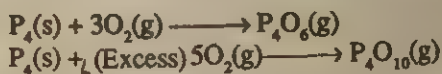
Table 13.2 includes the properties of atomic and molecular oxygen.

TABLE 13.2 Atomic and Molecular Properties of Oxygen

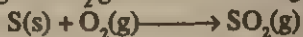
Atomic Properties		Molecular Properties	
Atomic radius (pm)	73	Melting point (K)	55
Ionic radius (O^{2-}) (pm)	140	Boiling point (K)	90
Electronegativity	3.5	Density (g/cm^3) at 298K	1.14
Electron affinity ($kJ\ mol^{-1}$)	141	Internuclear distance (pm)	120.7
Ionization energy ($kJ\ mol^{-1}$)	1314	Bond energy ($kJ\ mol^{-1}$)	493.4

1. Combustion of Non-Metals in Dioxygen

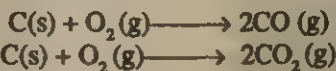
Dioxygen reacts directly with all other non-metals except the noble gases and the halogens. A small piece of burning phosphorus burns with a brilliant flame in the presence of dioxygen producing a dense white smoke of oxides.



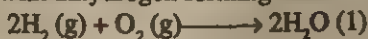
Sulphur burns with a pale blue flame much more brightly in the atmosphere of dioxygen to give SO_2 gas with a choking smell



A small lump of carbon heated to red heat glows more brightly in the presence of dioxygen forming carbon monoxide or carbon dioxide.

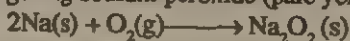


Dioxygen reacts readily with dihydrogen forming water.

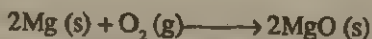


2. Combustion of Metals in Dioxygen

Active metals and some other metals burn in dioxygen. Noble metals such as gold, platinum, etc. are immune to dioxygen. A small piece of sodium, burning with a yellow flame, burns much more brightly in the presence of dioxygen giving sodium peroxide (pale yellow solid)



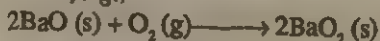
Preignited magnesium burns even more brightly forming a white powder of magnesium oxide.



Dioxygen combines slowly with copper and mercury on heating. It reacts spontaneously with lead (molten form), on heating, forming lead monoxide.

3. Combustion of Compounds in Dioxygen

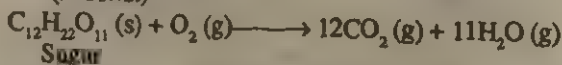
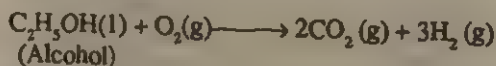
Many compounds when they are burnt or roasted in dioxygen form the oxides of their constituent elements. Sometimes dioxygen combines with the compounds as a whole, e.g.,



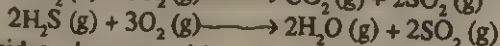
Hydrocarbons burn in dioxygen giving a mixture of carbon dioxide and steam.



Some other organic compounds form carbon dioxide and steam with dioxygen.



Carbon disulphide and hydrogen sulphide, when burnt in a plentiful supply of dioxygen, yield sulphur dioxide.

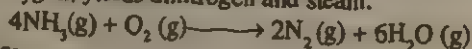


Metallic sulphides when roasted in air (or O_2) give sulphur dioxide and the metal oxide.

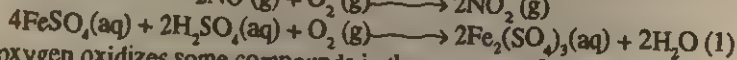
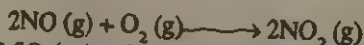


(This type of reaction is useful in the extraction of metals)

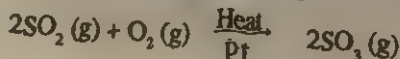
Dioxygen oxidizes some other compounds also. For example, ammonia, when burnt in oxygen, yields dinitrogen and steam.

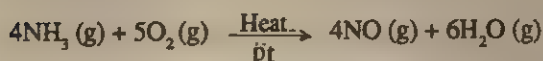
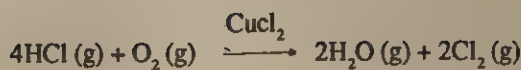


More examples:



Dioxygen oxidizes some compounds in the presence of a catalyst.





Some typical reactions of dioxygen are portrayed in Fig. 13.3.

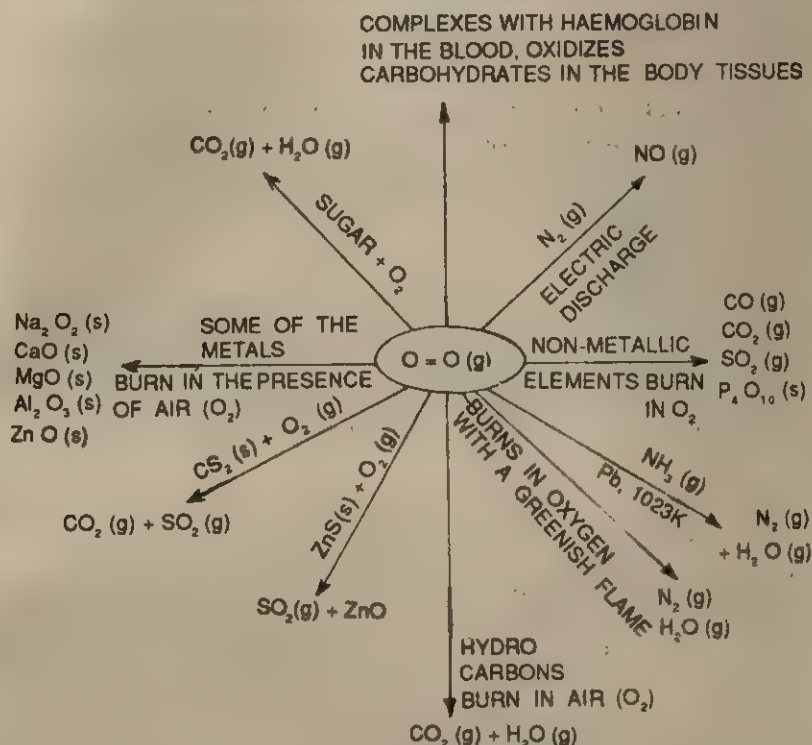


Fig. 13.3 Some Typical reactions of dioxygen.

13.3.6 Uses of Dioxygen

Most of the uses of commercial dioxygen are based upon its oxidizing nature. Some of the important uses are listed below:

1. In the manufacture of nitric acid, methyl alcohol, ethylene oxide and other chemicals.
2. As a propelling fuel in rockets, satellites, missiles, etc. in the form of liquid oxygen.
3. In oxy-acetylene torches for the high temperature welding and cutting of metals.
4. In bleaching and in thickening of oils used in making varnishes, linoleum, etc.
5. In making explosive cartridges by mixing it with carbon dust to be used in coal mining in place of dynamite.

6. Used in the production of steel because it removes carbon and other impurities more rapidly than air; also used in the extraction of metals.

7. Makes drinking water more palatable. Helps in destroying harmful bacteria and decaying animal and vegetable matter in soil, rivers and harbours by oxidation.

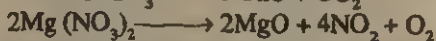
8. Used as an aid to respiration where the amount of dioxygen in air is insufficient, e.g., at high altitudes, in deep mines, in submarines, etc. Mountaineers, astronauts, deep sea divers and miners, etc. take self-contained oxygen equipment for breathing.

9. Used as an aid to respiration in medical and dental practice. It is supplied where lungs are weak or injury makes artificial respiration impracticable and in the resuscitation of victims of coal gas poisoning and other accidents. Dinitrogen oxide and other anaesthetics are administered along with dioxygen.

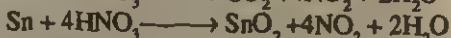
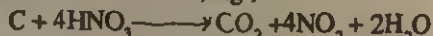
13.4 SIMPLE OXIDES

Almost all the elements form binary oxides. These oxides may be classified on the basis of their properties: (i) acid-base character, (ii) structure, (iii) nature of bond and so on.

The oxides of many non-metals and reactive metals can be obtained by direct combination with dioxygen. Thermal decomposition of hydroxides, carbonates and nitrates give oxides.



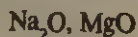
The oxides of some non-metals and weak metals are formed by the oxidation of element with nitric acid, e.g.,



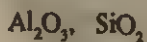
It is possible to arrive at four possible classifications of oxides on the basis of their acid-base properties: (i) Basic oxides, (ii) Acidic oxides, (iii) Amphoteric oxides, and (iv) Neutral oxides.

The acid-base character of an oxide depends upon the following:

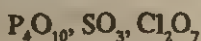
(a) The position of the element in the periodic table: Elements on the right in the periodic table (non-metals) form acidic oxides while those on the left form basic oxides (Fig. 13.4), i.e., there is a progression from strongly basic through amphoteric to strongly acidic.



Basic



Amphoteric



Acidic

(b) The oxidation state of the element: The higher the oxidation state, the more strongly acidic the oxide (most covalent state); lower oxides being successively more basic in character. This is explained well by oxides of chromium:

Chromium (II)

oxide, CrO, Basic

Chromium (III)

oxide, Cr₂O₃, Amphoteric

Chromium (IV) oxide, CrO_2 , Acidic

INCREASING ACIDIC CHARACTER \rightarrow

METALLOIDS

	Li	Be	B	C	N	O	F
	Na	Mg	Al	Si	P	S	Cl
	K	Ca	Ga	Ge	As	Se	Br
	Rb	Sr	In	Sn	Sb	Te	I
	Cs	Ba	Tl	Pb	Bi		

BASIC OXIDES AMPHOTERIC OXIDES ACIDIC OXIDES (EXCEPT CO , NO , N_2O , Fe_2O_3)

METALS

NON-METALS

INCREASING BASIC CHARACTER \downarrow

(PARTIAL SHADING EXHIBITS ONE OXIDE AMPHOTERIC WHILE THE OTHER IS BASIC OR ACIDIC)

Fig. 13.4 (i) Acidic and basic properties of the representative elements

(ii) Classification of the elements as metals, metalloids and non-metals on the basis of acid-base character of their group oxides.

(i) Basic Oxides

The basic oxides are those which have been shown by X-ray studies to contain discrete O^{2-} ions (present in normal oxides, e.g., MgO , SiO_2) in their crystal lattice. These oxides are mainly of two types:

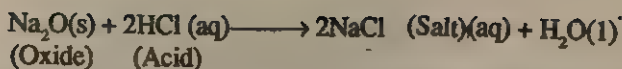
(a) those which react with water (e.g., CaO , Na_2O) producing $\text{OH}^-(\text{aq})$ —are generally simple ionic lattices containing O^{2-} ion, though some members of groups 1 and 2 form peroxides, $(\text{O} - \text{O})^{2-}$ and at times superoxides, $(\text{O} \cdots \text{O})^-$

(b) those which are insoluble in water (e.g., MgO , Al_2O_3 , SiO_2) usually dissolve in dilute acids.

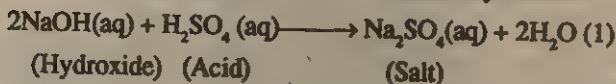


These oxides generally possess macromolecular structures in which the bonding is covalent.

Metals form ionic oxides which are basic in nature. Most of the oxides are solids with high melting and boiling points. They react with an acid to form a salt and water.



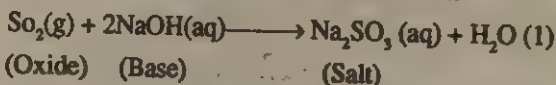
Also, the basic oxide reacts with water forming a hydroxide. The hydroxide itself also reacts with an acid to form a salt and water.



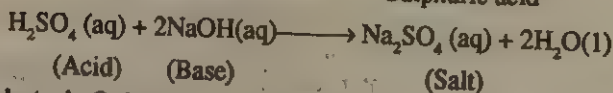
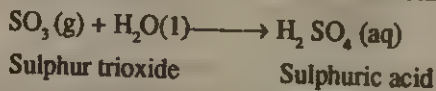
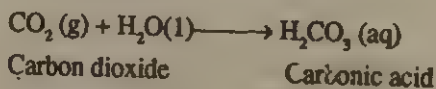
(ii) Acidic Oxides

Most non-metals form acidic oxides. They normally exist as covalent gases or liquids which attain molecular lattices in the solid state (e.g., SO_3 , CO_2). They react with water to form $\text{H}^+\text{(aq)}$.

Non-metals form covalent oxides which are either acidic or neutral. These oxides react with a base to form a salt and water.

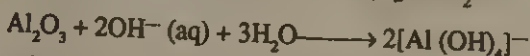
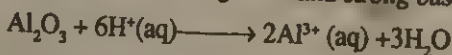


Most of the acidic oxides react with water to form the corresponding oxyacid. They may, therefore, be regarded as derived from acids by eliminating water; they are known as acid anhydrides. The acid itself reacts with a base to form a salt and water.



(iii) Amphoteric Oxides

These oxides react both with strong acids and strong bases:



Other examples are ZnO , SnO , SnO_2 , PbO , PbO_2 and Cr_2O_3 .

(iv) Neutral Oxides

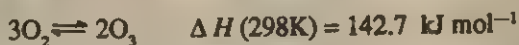
Some oxides e.g., N_2O , MnO_2 , OF_2 depict no acid-base properties. They are also termed as inert oxides.

Water, a simple compound, is an oxide of hydrogen and at the same time a hydride of oxygen. Its chemistry will be discussed later in this unit.

13.5 Ozone

Ozone, an allotrope of oxygen, plays a vital role in maintaining life on the earth because of its ability to absorb ultraviolet radiations. In the process of absorbing ultraviolet radiations, O_3 molecules decompose with the evolution of heat energy, and maintain the heat equilibrium in the atmosphere. Thus, it protects the earth and its inhabitants from the harmful ultraviolet radiations of the sun. Ultraviolet radiations cause damage to plant and animal life.

The formation of ozone from dioxygen is an endothermic reaction in which the energy may be furnished in the form of an electrical discharge, heat or ultraviolet light. At high altitudes (stratospheres, *i.e.*, the region of the atmosphere extending from the surface of the earth to an altitude of about 20 km), ultraviolet light from the sun dissociates some O_2 into atoms which in turn combine with dioxygen to form ozone.



When dry dioxygen is passed between the two electrically charged plates of an apparatus called 'Siemen's ozonizer' (Fig. 13.5), a pale blue gas, ozone having pungent odour is formed.

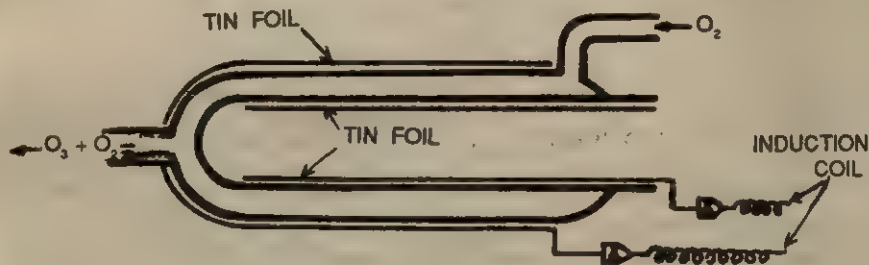


Fig. 13.5. Siemen's ozonizer for the preparation of ozone

Another apparatus used for the same purpose is called Brodie's ozonizer. In this apparatus, tin foils used in Siemens' ozonizer have been replaced by dilute H_2SO_4 (Fig. 13.6). The copper plates dipped into dilute H_2SO_4 are connected to an induction coil. Thus, dioxygen is subjected to silent electric discharge.

13.5.1 Properties and Reactions of Ozone

Ozone is a pale blue gas with pungent odour. It is liquefied to a deep blue liquid (b.p. 161.2K) which can be solidified to violet-black crystals

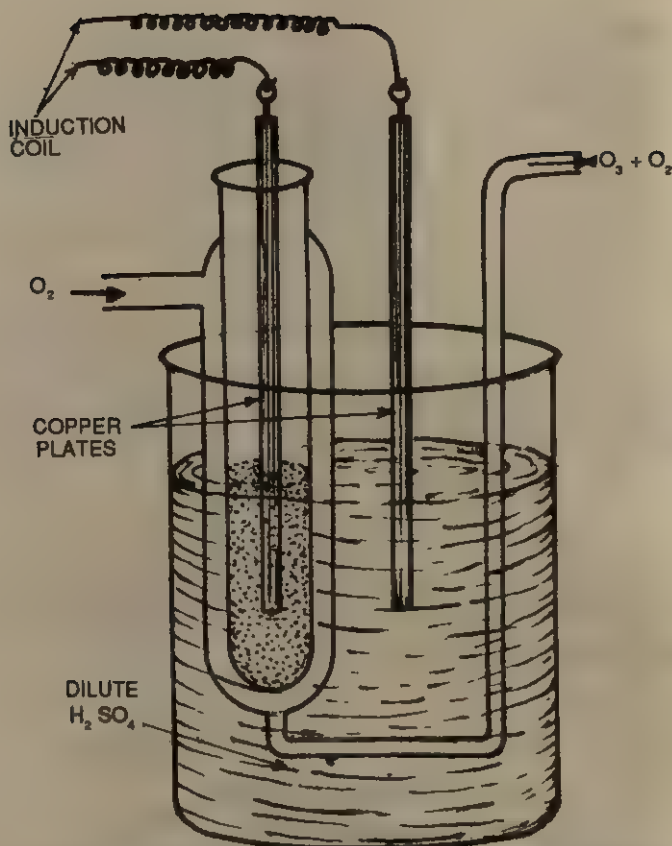


Fig. 13.6 Brodie's ozonizer for the preparation of ozone

(m.p. 80.6K). It is highly reactive and unstable (substances formed by endothermic reactions tend to be less stable than those formed by exothermic reactions). It is explosive at temperatures above 573K or in the presence of substances such as manganese dioxide or silver oxide, that catalyze its decomposition to dioxygen.

Ozone reacts with many substances at temperatures which are not high enough to initiate reaction with O_2 . Its high reactivity (more than O_2) is because of its higher energy content.

1. **Oxidizing Reaction:** O_3 is a stronger oxidizing agent than O_2

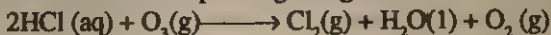
$$(O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O)$$

Thus, it oxidizes lead sulphide to lead sulphate, iodide ions to iodine and ferrous ions (II) to ferric ions (III).

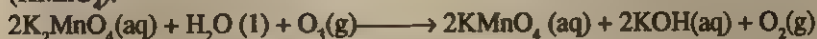


The oxidation of potassium iodide by ozone has been used for the estimation of ozone.

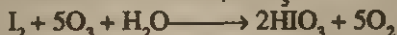
Silver and mercury are not attacked by air at ordinary temperatures whereas both are oxidized superficially in the ozone atmosphere. Halogen acids are oxidized to the corresponding halogens.



Potassium manganate (K_2MnO_4) is oxidized to potassium permanganate (KMnO_4).

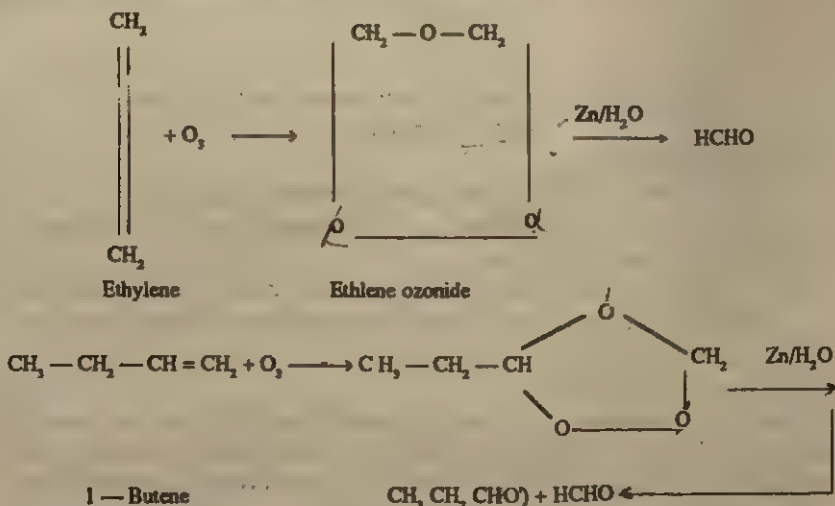


Moist iodine is oxidized to iodic acid, HIO_3 .



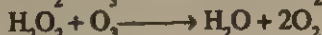
Dry iodine is, however, converted to a yellow powder, I_4O_9 . In a similar way moist sulphur, phosphorus and arsenic are oxidized to their corresponding oxyacids with the highest oxidation state.

2. Addition Reactions: Ozone adds on to unsaturated organic compounds forming ozonides. These ozonides are reductively cleaved by $\text{Zn/H}_2\text{O}$ producing aldehydes (or ketones). Ozonides can be decomposed by water or dilute acids producing aldehydes (or ketones) and H_2O_2 .

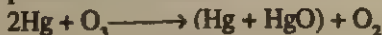


This reaction is known as 'ozonolysis'. The products obtained on hydrolysis help in fixing the position of the double bonds in unsaturated organic molecules.

3. Reaction with Peroxides: Ozone reacts with barium peroxide and hydrogen peroxide. During the reaction both peroxide and O_3 get reduced.



The oxidation of mercury causes mercury to tail (or stick to glass) and is used as a test for the presence of ozone.



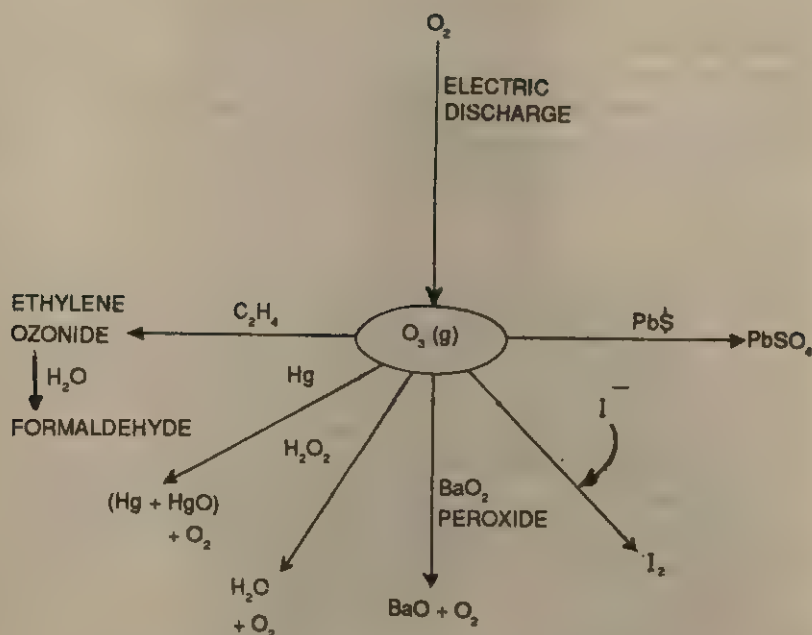


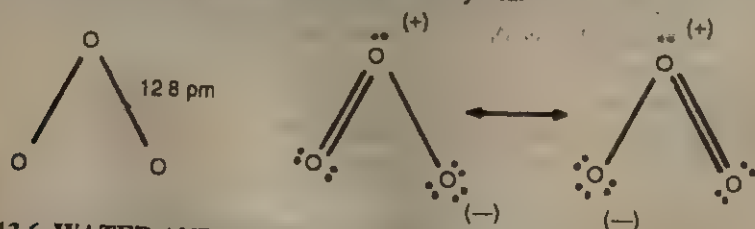
Fig. 13.7 Flow diagram for the preparation of ozone and its typical reactions

13.5.2 Uses of Ozone

1. Ozone is used as germicide and disinfectant to sterilize water.
2. It is used for the purification of air in crowded places - underground railways, mines, cinema halls, etc.
3. It is a mild bleaching agent - used to bleach wax, oils, starch, fabrics, etc. Its use as bleaching agent involves the oxidation of coloured materials to colourless compounds.

13.5.3 Structure of Ozone

Ozone is diamagnetic and has an angular structure. Both oxygen to oxygen bonds have the same length (128 pm) which is intermediate between the double bond distance (110 pm) and single bond distance (148 pm). The molecule may be represented as a resonance hybrid.



13.6 WATER AND HYDROGEN PEROXIDE

13.6.1 WATER

Water besides being plentiful and cheap is a highly interesting and

unique substance from chemical point of view. Water the most abundant liquid in the biosphere, is essential to all forms of life. Apart from being essential to life, it plays a very important part in the economy of a country. It is found everywhere on the earth in its various forms. Water fills depressions of the earth's crust to form lakes seas and oceans. It covers about 80% of the earth's surface. Huge accumulations of ice and snow cover the polar regions of the globe and peaks of high mountains. Water is always present in air in the form of vapours. Small water droplets form clouds that precipitate as rain to wet the soil and to feed springs, lakes and rivers. Thus, in nature water is found in all the three phases-solid, liquid, and gas.

TABLE 13.3 Water content in various systems

Systems	Water content by % mass
Oceans, lakes, rivers, etc	more than 95%
Human lives	about 70%
Trees	about 60%
Trapped in rocks (e.g. gypsum)	about 20%
Air	about 1-2%

Of the total estimated global water supply of $1.4 \times 10^9 \text{ km}^3$, the seas and inland saline water bodies hold 97.3% and fresh water amounts to 2.7%. Most of the fresh water is confined to frozen lakes, glaciers or under the ground. Only 0.003% of the total global water supply is available for human use.

Water never stays in one place for long. The heat energy warms oceans, streams, lakes and rivers and water evaporates into the atmosphere. When the air cools down, water vapours condense into water droplets which form clouds. When the droplets grow in size, they fall as rain or snow. Again, the water flows back into rivers, oceans, lakes, etc. completing a cycle called water cycle.

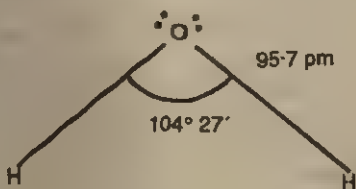
Water consists of two parts of hydrogen and one part of oxygen (Unit 10, electrolysis of water). Until the end of the 18th century, water was believed to be an element. Joseph Priestley got dew formed when he exploded a mixture of dihydrogen and air. But he thought this was due to water vapour present in air. Henry Cavendish repeated his experiments. As a result, he got a liquid assumed to be water. He delayed the publication of his results because of some inherent problems with the sample of water. Meanwhile, the French scientist, Lavoisier on the basis of his experiments - the burning of dihydrogen - realized that water must be a compound of hydrogen and oxygen. Lavoisier published this information without acknowledging his debt to the work of Cavendish.

Hydrogen peroxide (H_2O_2) is another hydride of oxygen which is very different from water in its properties. It was discovered by Thenard in 1818. It is formed in trace quantities by the action of sunlight on water containing dissolved dioxygen.

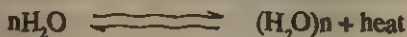
Structure of Water Molecule and its Aggregates

The characteristic properties of water - remarkable solvent, high boiling point, high heat of vapourization, and abnormally low vapour pressure - including the low density of ice are closely related to the structure of water molecule. These properties have a staggering influence biologically and environmentally.

Water molecule contains two hydrogen atoms joined to an oxygen atom by covalent bonds. In the vapour phase it is found in discrete form. Water is a V-shape molecule, the two bonding pairs and two lone pairs of electrons being arranged tetrahedrally round the oxygen atom. The structure of water molecule has been discussed in details in Unit 6. The atoms in the water molecule are held together by two polar bonds because of the electronegativity difference between oxygen and hydrogen. The molecule is polarized because of the high electronegativity of the oxygen atom, partial +ve charges (δ^+) residing on each hydrogen atom and a -ve charge (δ^-) on the oxygen atom.



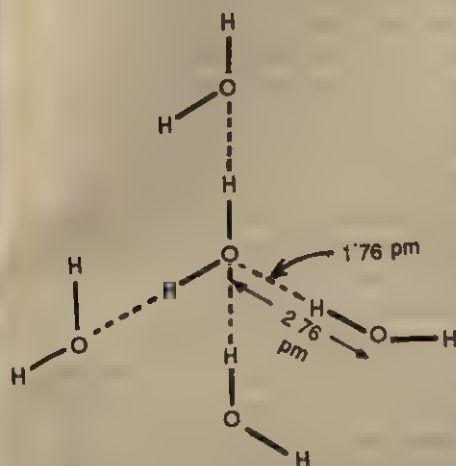
The oxygen atom of the water molecules can form two hydrogen bonds with the neighbouring two water molecules (Unit 6). Two hydrogen bonds are formed by association between the unbonded electron pairs on O-atom in H_2O and two hydrogen atoms from two other water molecules. The hydrogen bonds, even weak, are effective in producing associated molecules or polymers.



The value of n depends upon temperature and the presence of substances dissolved in water. The free water molecules are always in a dynamic equilibrium with the aggregate continually forming, collapsing and reforming. As the temperature is raised, some of the hydrogen bonds are disrupted and the large associated units are broken down into simpler ones. Association of water molecules is responsible for the distinct properties of

water listed in the beginning of this section. Abnormally low vapour pressure, high boiling point, high heat of vapourization and high heat of fusion of water as compared to the properties of non-associated hydrides of the group 16 arise by the fact that energy is required to break the hydrogen bonds holding the units together in the associated molecules.

Crystal chemistry has shown that water molecules in normal hexagonal ice are so arranged that each oxygen atom has four hydrogen atoms as close neighbours, two attached by electron pair bonds and two by hydrogen bonds (Fig. 13.8, Unit 6) : The distance between adjacent oxygen atoms is 276



pm, more than twice the O-H distance of ~ 96 pm in gaseous water molecules. Such an arrangement of water molecules in ice leads to an open structure which accounts for the fact that ice is less dense than water at 273K. When ice melts, the regular lattice breaks up and the water molecules can pack more closely and so the liquid has a higher density. As the temperature increases, the density increases gradually reaching a maximum at 277K. Thereafter, increasing thermal motion of molecules becomes more pronounced and the density decreases with temperature as seen with most of the liquids.

Fig. 13.8. The open structure of ice.

The fact that the ice is less dense than water at 273K means that lakes, ponds, etc. freeze from the surface downwards and the layer of ice insulates the water below, preventing complete solidification. Because of its low density, ice floats on water. This delays the freezing of underlying water and thus fishes, aquatic plants and other water-living creatures survive during the winter months.

Physical Properties of Water

Pure water is an odourless, tasteless and colourless liquid. Natural waters have a bluish green colour in large bodies. Its pleasant taste is due to dissolved gases from the air and salts from the earth.

The freezing point of water is 273K and its boiling point at 760 mm Hg is 373K. Water is a polar solvent; it is equipped with the property of high dielectric constant of being able to dissolve many ionic solids. Because of the polar nature of water, plants can acquire the salts, their which they require for their growth, by absorbing these materials into the sap through their roots. Animals absorb substances (polar and ionic materials required for growth) into their blood stream from the aqueous solution in their stomachs and intestines.

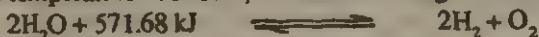
Water also dissolves a number of molecular substances, e.g. sugars and alcohols because of their ability to form hydrogen bonds with water molecules. Without the existence of these H-bonds, water would probably be a gas under normal atmospheric conditions ; seas, lakes and rivers would never exist and it would never rain. Hydrogen bond also causes higher surface tension and high viscosity. Were it not for this, water would never rise through the capillary tubes in the roots and stems of the plants.

Apart from the properties discussed earlier, water has high specific heat and thermal conductivity. These properties including surface tension are responsible for water to play a vital role in the biosphere. The high heat of vapourization and the high heat capacity of water have a bearing effect on the climate and body temperature of living organisms.

In fact, presence of hydrogen bond in the condensed phase of water is responsible for all the peculiarities and potentialities associated with water. Table 12.3 (Unit 12) gives the comparison of some of the properties of liquid water and its deuterium analogue.

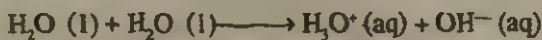
Chemical Properties of Water

1. **Thermal Stability :** Water exhibits a high thermal stability because its heat of formation is very high. It decomposes to the extent of 11.1% at the very high temperature of 3000K, the reaction being reversible.



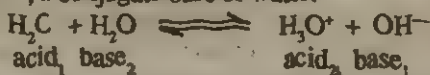
As the temperature is decreased, the constituent elements recombine. The extent of dissociation at 1500K is < 0.02%. Although water is stable toward decomposition by heat, it is a very reactive substance and is involved in a variety of reactions, even at ordinary temperature.

2. **Ionization of Water :** Pure water conducts electricity, but very poorly, because it ionizes into hydrated hydrogen ions (H_3O^+) and hydroxyl (OH^-) ions.



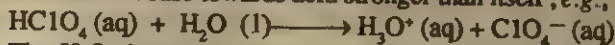
$$K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2} \text{ at } 298\text{K}$$

This ionization of water is obvious because water being obtained in the neutralization reaction of an acid and a base. Its neutral nature subscribes to its poor dissociation. The isolated H^+ ion does not exist free in solution but combines with a water molecule to form the hydrated ion called the hydronium ion, H_3O^+ . Thus, water itself is both a Bronsted acid and a base. Hence, the autoionization of water is an acid-base reaction according to the Bronsted Lowry concept. One H_2O molecule (the acid) donates a proton to another H_2O molecule (the base). In the process, water molecule the donor of H^+ becomes OH^- , a conjugate base of water.



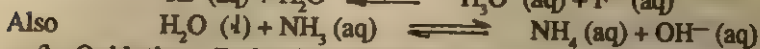
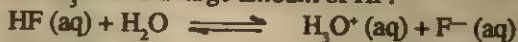
The H_2O molecule that accepts a proton in turn becomes H_3O^+ . The signs of reversible indicates that H_3O^+ (an acid) donates a proton to OH^- (a base) to form two H_2O molecules. Thus, water is amphoteric in nature.

Water acts as a base towards acid stronger than itself, e.g.,



The H_2O is a stronger base, and thus, accepts the proton which leaves H_3O^+ as the only acid remaining in the solution.

If the acid is a weaker acid than H_3O^+ , as is HF , two acids would result - a small amount of H_3O^+ and a large amount of HF .



3. Oxidation - Reduction Reactions : Apart from acid - base reactions, oxidation - reduction reactions also take place in aqueous solution. Some of the metals whose E° value of the redox couple M^{n+}/M is below -0.41 V reduce water.



$$E^\circ = 41 \text{ V for } [\text{OH}^-] = 10^{-7} \text{ M}$$

Some other metals/species whose E° value of the redox couple M^{n+}/M is above -0.41 V oxidize water,



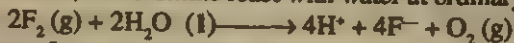
Thus, water itself can act both as an oxidizing and reducing agent.

Many metals displace dihydrogen from water (preparation of dihydrogen). The more active metals react with cold water and the less active ones require steam.

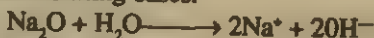


Magnesium reacts with hot water forming $\text{Mg}(\text{OH})_2$ and dihydrogen.

Fluorine, chlorine, and bromine react with water at ordinary temperature.

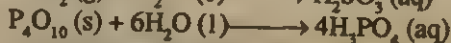
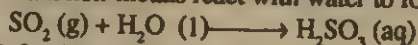


4. Reaction of water with compounds : The oxides of alkali metals react readily with water forming bases.

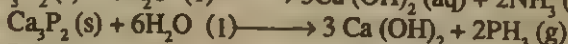
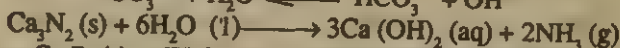
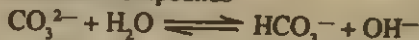


The oxides of alkaline earth metals react less readily.

The oxides of certain non-metals react with water to form acids.

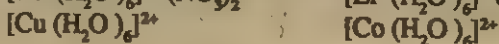
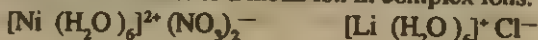


Water hydrolyses certain compounds



5. Hydrates formation : Because of its lone pair of electrons, water is capable of forming some compounds with metal salts known as hydrates. They are of three types.

(a) Water molecules coordinate to a metal ion in complex ions.



(b) Water molecules are bonded to certain oxygen containing anions e.g., $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Here four water molecules are coordinated to the central atom of Cu^{2+} and the fifth H_2O molecule is hydrogen bonded to a sulphate group. The hydrate, most frequently used in medicine, is plaster of paris, $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$.

(c) Water gets trapped in certain voids (interstitial sites) in the crystal lattice, e.g., $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.

13.6.2 Hydrogen peroxide

Hydrogen peroxide, H_2O_2 a molecular hydride of oxygen contains structural units $(\text{O}-\text{O})^{2-}$. It was first prepared in 1818 by Thenard who obtained it by treating barium peroxide with hydrochloric acid.

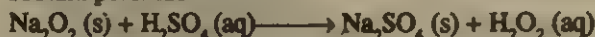
Preparation of Hydrogen Peroxide

Hydrogen peroxide can be successfully obtained by adding ice cold dilute acid to:

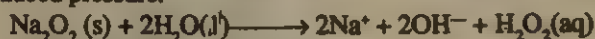
(a) hydrated barium peroxide



(b) sodium peroxide

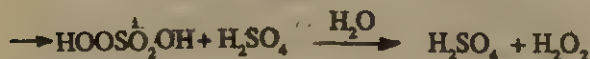
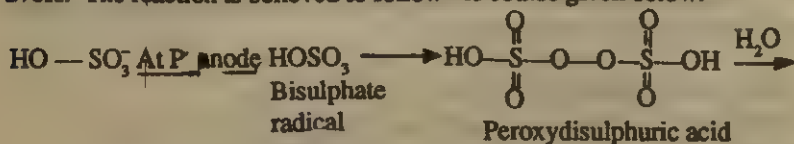


Barium sulphate is insoluble and can be separated from the solution by filtration. Hydrogen peroxide is generally prepared in the laboratory by adding sodium peroxide to cold water or dilute HCl. The H_2O_2 produced in these methods is quite dilute which can be concentrated by distillation under reduced pressure.



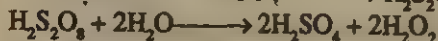
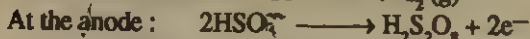
Industrial methods include,

(a) **Electrolysis of sulphuric acid solution or ammonium sulphate at 278K.** The reaction is believed to follow the course given below:



Peroxydisulphuric acid

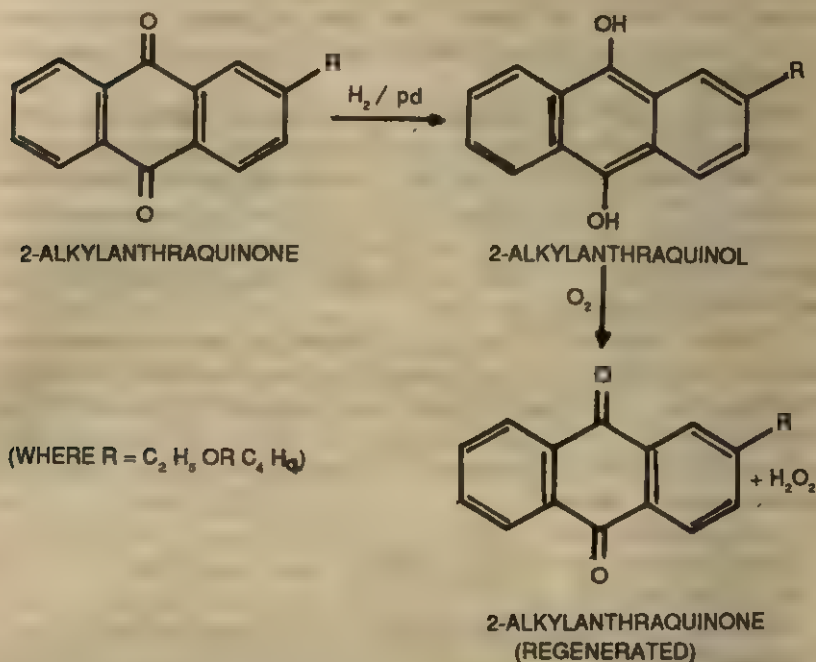
The electrolysis of solutions of H_2SO_4 leads to produce peroxydisulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$ at the anode and hydrogen at the cathode. The peroxydisulphuric acid is subsequently hydrolysed to form hydrogen peroxide.



The sulphuric acid formed is recycled, i.e., it is used over again in the production of H_2O_2 .

The product obtained is generally 30-35% aqueous solution, but 90% is obtained commercially by fractional distillation under reduced pressure.

(b) The auto-oxidation of an organic compound anthraquinol in benzene and long chain alcohols.

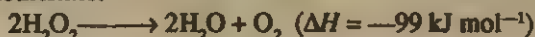


The product is generally extracted with water. It is usually 18-20% aqueous solution, but 90% is obtained by fractional distillation under reduced pressure at 333K. High concentration can be obtained by fractional crystallization (at low temperature pure crystals are deposited).

The anthraquinone produced in the reaction is used again in the production of hydrogen peroxide.

Properties and Reactions of Hydrogen Peroxide

Very pure H_2O_2 is quite stable. Pure H_2O_2 is faintly blue. The liquid is polar and is an associated substance like water owing to the presence of H-bonding. It decomposes violently when heated, the reaction being exothermic.



Aqueous solution remains stable in the presence of acid or acetanilide (stabilizer).

Hydrogen peroxide readily decomposes to give dioxygen and water. The decomposition is catalyzed by metal impurities (e.g. heavy metals like Ag, Au, Pt, and metal ions Fe^{2+} , Cu^{2+} and metal oxides MnO_2), strong base and

sunlight. Because of this property, concentrated solutions of H_2O_2 are never stored as it could be dangerous. This property supports the use of reduced pressure when concentrating the aqueous solution. It is stored in coloured wax-lined bottles in the presence of a stabilizer. It has a density of 1.438 g/cm^3 at 293K , boils at 336K at 21mm Hg and freezes at 271.5K . It is not possible to determine its boiling point at atmospheric pressure as it decomposes violently on heating. The estimated normal boiling point is 423.2K . It is miscible (mutually soluble) with water, alcohol and ether in all proportions.

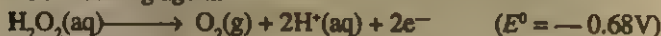
Its unstable nature is attributed to the fact that its formation is highly endothermic in nature. Hydrogen peroxide is usually sold as 20 volume solutions, meaning that 1 volume of the solution will provide 20 volumes of oxygen at STP. From the equation $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2 + \text{O}_2$ it can be seen that 2 moles of H_2O_2 give 1 mole of O_2 i.e., 68g of H_2O_2 give $22.4 \text{ litre (dm}^3\text{)}$ of O_2 at STP. It is, therefore, possible to calculate the volume strength of H_2O_2 if its molarity is known and vice-versa.

Chemical Reactions: Hydrogen peroxide acts both as an oxidizing agent and a reducing agent in both acidic and alkaline solution. In all its oxidizing reactions, it has an advantage over other oxidizing agent because it is always reduced to water. The oxidation state of oxygen in H_2O_2 is -1 . It is oxidized to O_2 (Zero oxidation state) or reduced to H_2O or OH^- (-2 oxidation state for oxygen).

As an oxidizing agent:

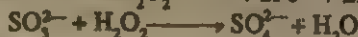
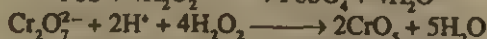
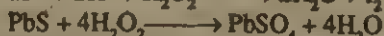
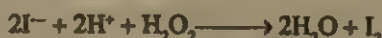


As a reducing agent:



Oxidizing Reactions

In acid solution:

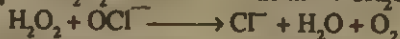


In alkaline solution:

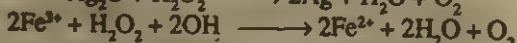


Reducing Reactions

In acidic solution"



In alkaline solution



Acidic solution favours the oxidizing action, e.g., Fe^{2+} to Fe^{3+} ; PbS to PbSO_4 ; I^- to I_2 .

Hydrogen peroxide reduces MnO_4^- to Mn^{2+} even in acidic solution.

Uses of Hydrogen Peroxide

Hydrogen peroxide has a variety of uses as an oxidizing agent, a bleaching agent and a rocket fuel in conjunction with liquid hydrazine. Other uses include the preparation of peroxides, particularly organic peroxides which are used for initiating polymerization reactions and the preparation of antiseptics. It is also used in the manufacture of sodium perborate and epoxides. It is used in the laboratory as an aqueous solution. Oxidizing reactions, in particular, are very useful. Old paintings are restored (white lead paint slackens by traces of H_2S in the atmosphere). Oxidation of acidified dichromate (CrO_5 is extracted with ether) serves as a qualitative test for Cr. Many dyes are bleached by oxidation with H_2O_2 ; textiles, wood pulp, toothpastes, etc., are bleached in this way.

Recently it has found its use in controlling of pollution. Domestic and industrial effluents, e.g., cyanides and other obnoxious sulphides are oxidized by H_2O_2 .

Structure of Hydrogen Peroxide

The hydrogen peroxide molecule contains two $\text{O}-\text{H}$ groups, which do not lie in the same plane, joined together through the two oxygen atoms. In the gas phase, the molecule adopts a skew configuration with a dihedral angle of 111.5° as shown in Fig. 13.9a because of the repulsive interaction of the $-\text{OH}$ bonds with the lone pairs of electrons on each 'O' atom. This is the most stable configuration because the repulsion between the two lone pairs of electrons on the two oxygen atoms is minimum. The skew form persists in the liquid phase with some modifications caused by H-bonding. In the crystalline state, H_2O_2 assumes the dimensions as suggested through Fig. 13.9b. The dihedral angle is particularly sensitive to H-bonding, decreasing from 111.5° in the gas phase to 90.2° in crystalline H_2O_2 .

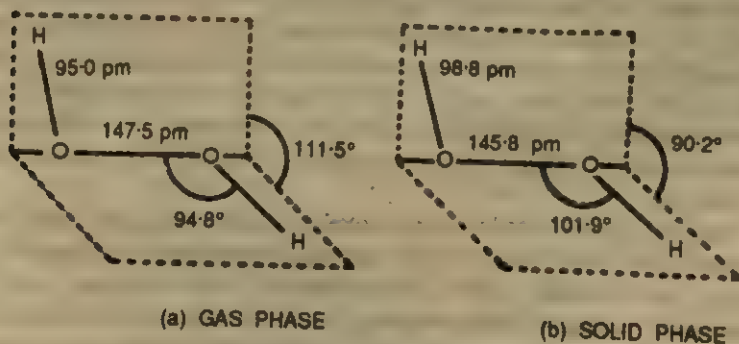


Fig. 13.9 Structure of H_2O_2 molecule as in the gas phase, and (b) in the crystalline state.

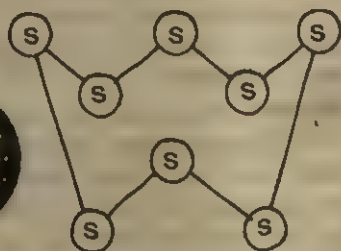
13.7 SULPHUR

• Sulphur has been known since early times, being used by Egyptians and the Greeks as a yellow colouring material. Alchemists tried to incorporate its 'yellowness' into other substances in attempts to produce gold. Lavoisier recognized sulphur as an element in 1777.

Because of its occurrence near volcanoes, sulphur commanded the awe of ancient man. Sulphur has been proved to be one of the cornerstones of chemical technology, mainly because of the industrial importance of sulphuric acid and the agricultural importance of sulphate fertilizers.

Sulphur has 6 electrons in its valence shell. It tends to add two electrons to form S^{2-} ions or form two covalent bonds to attain its octet of electrons. The atoms of sulphur usually do not multiple bonding like oxygen, sulphur in the solid state exists as S_8 which assumes the puckered ring structure.

The S_8 rings also persist in the liquid and gaseous states.



PUCKERED RING STRUCTURE

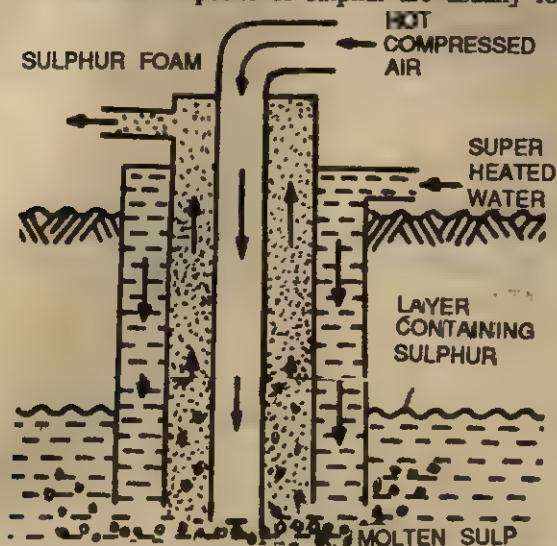
13.7.1 Occurrence

Sulphur is found extensively in the earth's crust (0.05%) both in the free elemental state and in the combined state. Free sulphur occurs in large natural deposits near volcanoes and can be mined without further purification. The large sulphur deposits occur near the Gulf of Mexico and in Sicily. Its deposits are also found in Japan, Italy and USA (Texas and Louisiana). In the combined state, sulphur occurs as sulphides (iron pyrites, FeS_2 ; galena, PbS ; zinc blende, ZnS ; copper pyrites, $CuFeS_2$; etc.) and sulphates (barite, $BaSO_4$; gypsum, $CaSO_4 \cdot 2H_2O$) of metals. To some extent it also occurs in volcanic gases as hydrogen sulphide, H_2S and sulphur dioxide, SO_2 .

Sulphur is also a constituent of naturally occurring organic matter such as petroleum (in the form of H_2S) and coal. Its presence in fossil fuels causes environmental and health problem because sulphur and its compounds undergo combustion giving sulphur dioxide, an air pollutant. It is also present in various forms in plants and animals. It is present in garlic mustard, egg, protein, oils, etc.

13.7.2 Extraction of Sulphur

Since the deposits of sulphur are usually found at a depth of 150-200



metres below the surface of the earth, under the layers of quicksand and gravel, this makes its direct mining impossible. It is extracted by the Frasch method (Fig. 13.10). Three concentric pipes are sunk to reach the deposits. Superheated water (440k) under pressure is forced down the outer pipe and compressed air is blown down the central

shaft (inner-most pipe). Water melts the sulphur. The molten sulphur forms a froth with the compressed air. The compressed air also forces up this froth to the surface through the middle-pipe. It is then allowed to cool and solidify into vats. Sulphur so obtained is of about 99.9% purity. This method is used in USA.

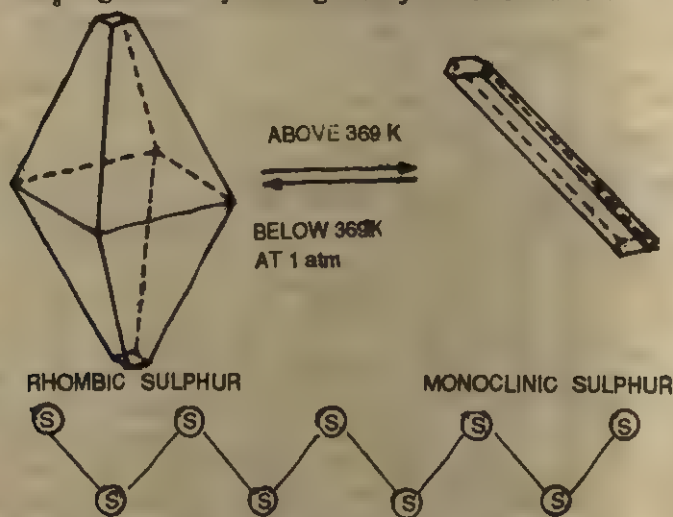
Small amount, but a highly pure sample of sulphur can be obtained by burning hydrogen sulphide in a limited supply of air. Sulphur so produced is used to manufacture sulphuric acid and other industrially important products. Sulphide ores on heating give sulphur dioxide which can be converted directly to sulphuric acid.

13.7.3 Allotropy in sulphur

Sulphur can exist in several allotropic forms. There are perhaps over a dozen different sulphur allotropes. The most common of the well-characterized sulphur allotropes are the orthorhombic and monoclinic forms. Both contain covalently bound S_8 puckered rings, the difference in the allotropes being a difference in the crystal packing of the S_8 units (Fig. 13.11). Orthorhombic sulphur, the most stable form at ordinary temperature, changes to the monoclinic above 369K. However, the inter-conversion between the two forms is slow depending upon the temperature. This kind of allotropy is described as enantiotropic (moving in both directions). These two forms are soluble in non-polar solvents such as benzene, carbon disulphide, ether and alcohol.

A third unstable but important allotrope is called plastic sulphur. This is an amorphous solid obtained from a supercooled liquid. This is a sticky elastic substance which can be drawn into long threads. It contains long

helical chains of sulphur atoms (Fig. 13.11). It is insoluble in non-polar solvents. After a few days the long chains slowly disintegrate and reform the small S_8 rings which crystallize gradually in rhombic lattice.



PLASTIC SULPHUR—COMPOSED OF HELICAL CHAINS

Fig. 13.11 Allotropes of sulphur

A comparison of the physical properties of the allotropes of sulphur is given in Table 13.4.

Sulphur parallels with phosphorus in its ability to form a wide variety of allotropes in all the three phases. All the forms are not fully established. The interrelationship among the various forms of sulphur is given in Fig. 13.12.

TABLE 13.4 Physical properties of allotropes of sulphur

Property	Rhombic	Monoclinic	Plastic
Colour	Pale yellow	Yellow	Yellowish-brown
State	Octahedral crystals	Needle like crystals	Rubber like mass
Melting point, (K)	387.5	392	No definite m.p.
Density (g/cm^3)	2.06	1.98	1.95
Solubility in CS_2	Soluble	Soluble	Insoluble

13.7.4 Properties and reactions of sulphur

Sulphur is a pale yellow solid with no odour. It is insoluble in water. It

is soluble in carbon disulphide, acetone, and carbon tetrachloride. Sulphur burns in air with a blue flame forming sulphur dioxide. When crushed roll sulphur (commercial form) is heated in the absence of air it melts and then undergoes a set of changes (Fig. 13.13).

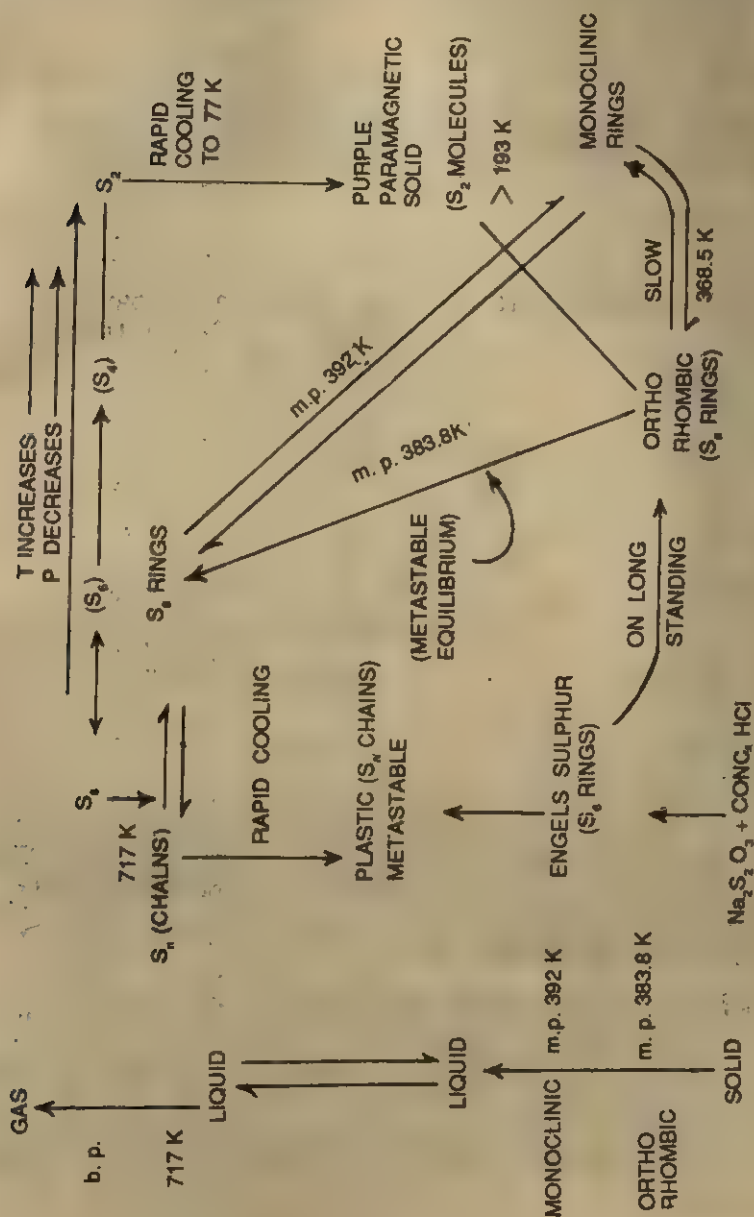


Fig. 13.12 The interconversion of the allotropes of sulphur.

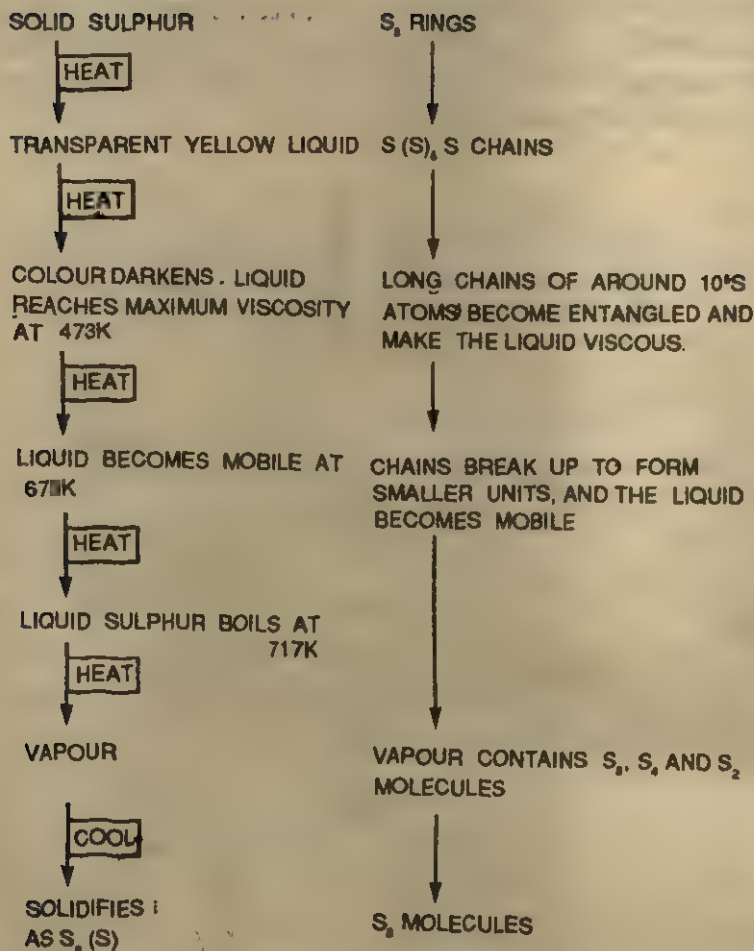
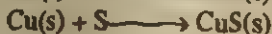
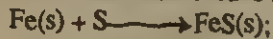


Fig. 13.13 The changes that occur when sulphur is heated.

1. **Reaction with metals:** Sulphur combines with many metals except tellurium and noble metals (e.g. gold, platinum) giving sulphides on heating.



Sulphides on reacting with dilute acids, e.g., HCl, H₂SO₄, etc. give hydrogen sulphide, H₂S, a foul smelling poisonous gas.

2. **Reaction with non-metals:** Various non-metals that react with burning (or preheated) sulphur include fluorine, chlorine, bromine, dihydrogen, dioxygen, carbon, phosphorus, etc. It reacts less readily with non-metals than dioxygen. Noble gases, iodine and dinitrogen do not react with sulphur.



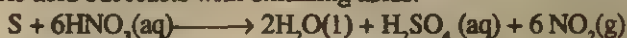
(Excess)



(Excess)



3. **Reaction with acids:** Sulphur does not react with aqueous hydrochloric acid but reacts with oxidizing acids.



4. **Reaction with alkalis:** Sulphur reacts with hot concentrated solutions of alkalis giving sulphides and sulphites.

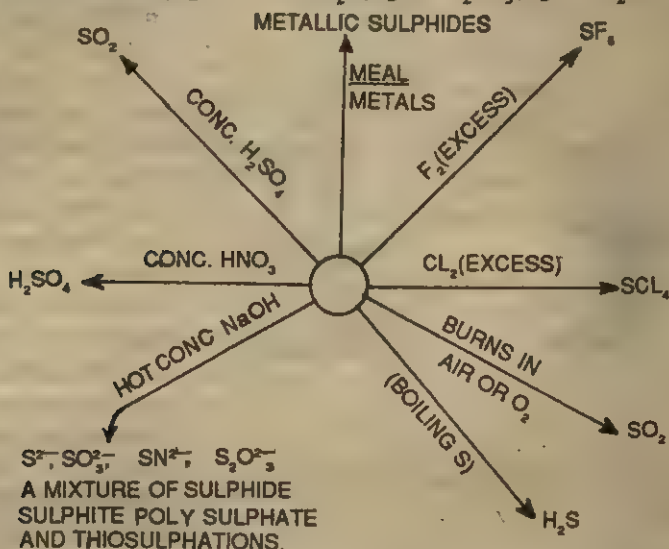
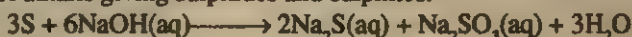


Fig. 13.14 Flow diagram for typical reactions of sulphur

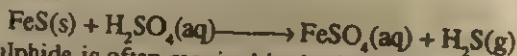
13.7.5 Uses of sulphur

Sulphur is widely used: (i) in the manufacture of sulphur dioxide and sulphuric acid, (ii) to produce vulcanised rubber, (iii) in producing important chemicals. These include carbon disulphide, sulphur dyes, calcium and magnesium bisulphites (bleaching agents), phosphorus trisulphide (used in match industry) etc., (iv) in the manufacture of explosives, e.g., gunpowder (sulphur, carbon and potassium nitrate) and fireworks. (v) as a germicide and insecticide for controlling growth of fungus in plants and (vi) in medicines and in ointments for treating skin diseases and for manufacturing sulpha drugs. Sulphur and its compounds are commonly used in the Ayurvedic system. Mercuric sulphide is used as an Ayurvedic medicine under the name of Makaradhwaj

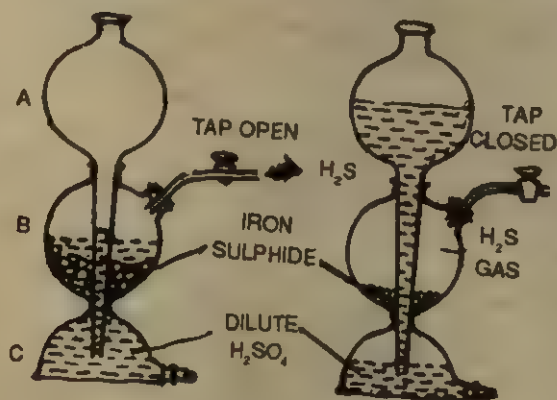
13.8 COMPOUNDS OF SULPHUR

13.8.1 Hydrogen Sulphide

Hydrogen sulphide is an important compound of sulphur with hydrogen. It is usually prepared by the action of dilute hydrochloric or sulphuric acid on iron (II) sulphide.



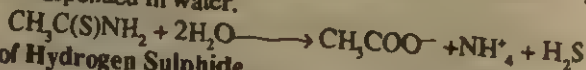
Hydrogen sulphide is often required in the laboratory. For this purpose, the gas is usually prepared in a Kipp's apparatus (Fig. 13.15). When the tap



T is opened, the acid rises into the compartment B. Here the acid reacts with iron sulphide to produce H_2S . The gas is taken out through the side tube. When the apparatus is not in use, the tap T is closed. On closing the tap, the pressure of the gas in compartment B increases. As a result, the acid goes back into the compartment A through compartment C, and the production of the gas stops.

Fig. 13.15 Continuous supply of H_2S gas in the laboratory.

Hydrogen sulphide can be generated directly in solution by heating thioacetamide suspended in water.

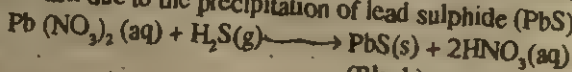


Properties of Hydrogen Sulphide

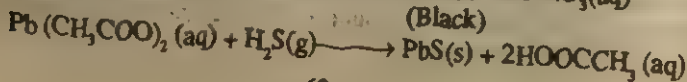
Hydrogen sulphide, has characteristic repulsive odour like that of rotten eggs. It is colourless and poisonous in nature.

1. **Acidic Nature:** It is fairly soluble in water and its solution is weakly acidic in nature.

2. **Reaction with Metal Salt Solutions:** It reacts with many salt solutions forming insoluble coloured sulphides. Some sulphides are precipitated in acidic medium and some others are precipitated in alkaline medium. When H_2S is bubbled through a solution of lead acetate or lead nitrate it turns black due to the precipitation of lead sulphide (PbS).



(Black)



In a similar fashion, H_2S reacts with other metal salt solutions,

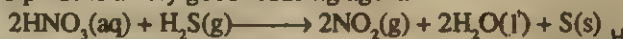
In acidic medium



In alkaline medium



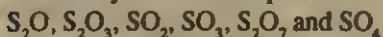
Such reactions of hydrogen sulphide are used in qualitative inorganic analysis for identifying the various metallic ions. Most of the sulphides are insoluble in water except those of groups 1 and 2. The solubility of the sulphides can be controlled by the H^+ ion concentration in solution. Hydrogen sulphide is a very good reducing agent.



Its boiling point is much lower than that of water indicating that the effect of molecular association is more in the case of water. It has an angular shape similar to that of water.

13.8.2 Oxides of Sulphur

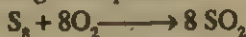
The binary oxides of sulphur are:



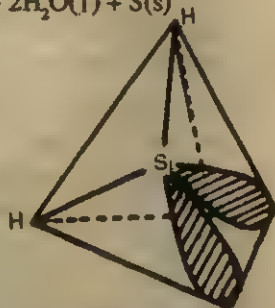
Of these, sulphur dioxide and sulphur trioxide are the most important.

Sulphur dioxide is an important gas which is used mainly for the manufacture of sulphuric acid. It occurs in volcanic gases. Many hot springs contain dissolved sulphur dioxide. Atmospheric air also contains traces of this gas which is released into the atmosphere from coal and oil based power plants, oil refinery operations and during the roasting of metallic sulphides. Atmosphere over industrial towns is rich in sulphur dioxide. This gas is one of the major air pollutants.

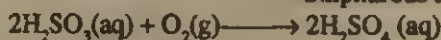
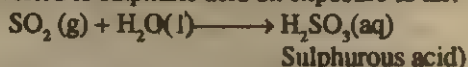
For commercial purposes, the gas is obtained by burning sulphur in air or as a byproduct from the roasting of sulphides.



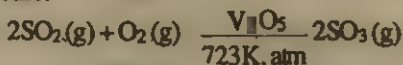
Sulphur dioxide is a colourless gas with a sharp choking smell of burnt sulphur. It is poisonous and causes inflammation of the lungs and other



disorders. It is heavier than air and highly soluble in water. It can be readily liquefied. Its aqueous solution is acidic in nature. The solution so obtained is of sulphurous acid, H_2SO_3 . This acid is unstable. It only acts in situ. It is slowly converted to sulphuric acid on exposure to air.

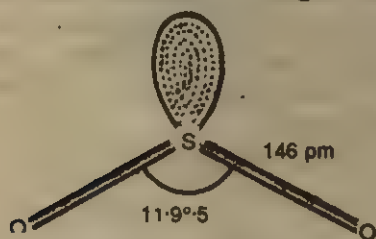


Sulphur dioxide combines with dioxygen in the presence of a platinized asbestos or vanadium pentoxide at a temperature of about 723K and at one atmospheric pressure.



It behaves both as reducing and oxidizing agent. It can bleach the colours of the substances because of its reducing nature.

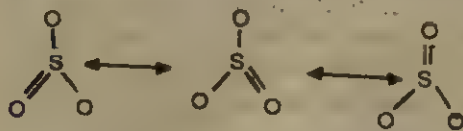
Sulphur dioxide is an angular molecule with an O-S-O angle of 119.5°



and a high dipole moment of 1.6 debyes. The S-O bond length of 146pm indicates some double bond character in the molecule. The structure of SO_2 probably involves resonance. It involves sp^2 disposition about sulphur atom.

STRUCTURE OF SULPHURDIOXIDE, SO_2

Sulphur trioxide is formed by the direct oxidation of SO_2 with atmospheric dioxygen at elevated temperature (673-973K). It is an extremely reactive substance and a strong oxidizing agent. It is the anhydride of H_2SO_4 and reacts violently with water to produce the acid and with metallic oxides to produce sulphates. It dissolves in concentrated H_2SO_4 forming pyrosulphuric acid, $\text{H}_2\text{S}_2\text{O}_7$ (fuming sulphuric acid or oleum). At temperature of 1173K or higher, SO_3 decomposes to SO_2 and O_2 .



STRUCTURE OF SULPHUR TRIOXIDE, SO_3

Sulphur trioxide gas has a planar triangular structure, with S-O distance of 142 pm. It involves sp^2 hybridization about sulphur atom. The molecule is symmetrical and has no dipole moment.

13.8.3 Sulphuric acid

Sulphuric acid is a substance of great industrial importance and the industrial prosperity of any country is closely related to its sulphuric acid consumption. It is the most common oxyacid of sulphur. It is called 'king of chemicals' because of its extensive use in industries. Following are the

key industries of India, where sulphuric acid is manufactured:

1. Hindustan Zinc Limited, Debari and Vishakapatnam,
2. Hindustan Copper Limited, Khetri and Ghatsila,
3. Fertilizer Corporation of India, Sindri, Bihar
4. DCM Chemical Works, Delhi.

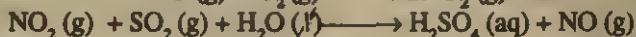
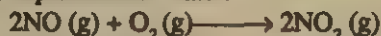
Manufacture of sulphuric acid

Essentially the manufacture of sulphuric acid, H_2SO_4 involves the conversion of SO_2 to SO_3 which is then processed further.

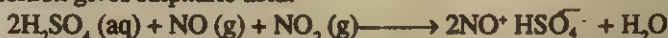
There are two main industrial processes for the manufacture of H_2SO_4 from SO_3 .

1. The contact process
2. The lead chamber process

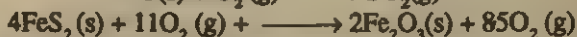
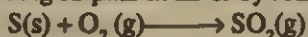
The lead chamber process is an older method for the manufacture of H_2SO_4 . In this process oxidation of SO_2 is effected catalytically by means of oxides of nitrogen in the presence of water.



The unreacted gases (NO , NO_2 and O_2) are absorbed in H_2SO_4 and nitrosyl sulphuric acid (nitrosyl bisulphate) is formed. This on decomposition gives sulphuric acid.

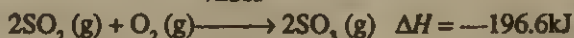


Most of the H_2SO_4 used today is produced by the **contact process** in which SO_2 is catalytically oxidized to SO_3 . Sulphur dioxide for the purpose is usually obtained by burning sulphur in air or by roasting iron pyrites.



Chemical principle of the contact process: Purified SO_2 is oxidized to SO_3 catalytically (platinized asbestos or vanadium pentoxide; vanadium pentoxide is more resistant to poisoning) with atmospheric dioxygen at a temperature of about 723K and at atmospheric pressure. The reaction is exothermic and the temperature rises to about 873K.

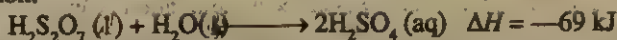
723K



The SO_3 vapours are absorbed in concentrated H_2SO_4 (98-99%) and pyrosulphuric acid ($\text{H}_2\text{S}_2\text{O}_7$) is formed. Pyrosulphuric acid is a fuming liquid called 'Oleum'.



Water is then added to oleum to make sulphuric acid of the desired concentration.



Conditions for maximum yield: The oxidation of SO_2 is reversible, exothermic and proceeds with decrease in volume. The optimum conditions for a better yield in accordance to 'Le Chatelier's principle' are:

1. **Low temperature:** The oxidation of SO_2 to SO_3 is exothermic, and hence, is favoured by low temperature. The reaction is too slow to be commercially feasible at low temperature. Hence, the oxidation is carried out catalytically at about 723K. A yield of about 90% is obtained at this temperature.

2. **High pressure and excess of oxygen:** High pressure favours the oxidation step. However, at high pressure, the material of the plant is liable to be corroded. The reaction is carried out in the presence of excess of oxygen and at atmospheric pressure for better yield of sulphur trioxide.

The essential stages in the manufacture of sulphuric acid are shown diagrammatically in Fig. 13.16a. The integrated diagram for the manufacture of sulphuric acid by contact process is shown in Fig. 13.16b. Broadly it consists of the following units.

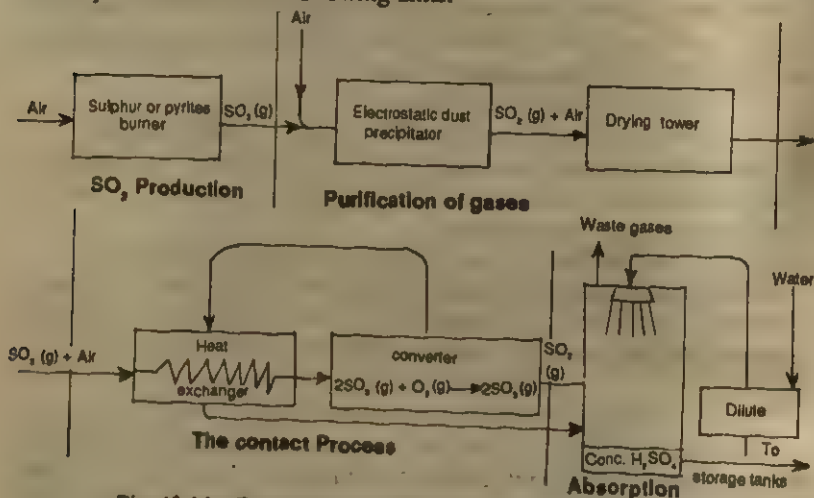


Fig. 13.16a Essential stages in the manufacture of sulphuric acid

(a) Sulphur or pyrites burners

(b) Purifying assembly and testing box: The hot gases emanating from the burner unit are usually found mixed with certain impurities like oxides of arsenic (As_2O_3), sulphur or dust particles, etc. The impure hot gases are first passed through an electrostatic precipitator and then are washed with water to remove soluble impurities.

(c) Contact chamber or converter: Firstly, the purified gases are heated by passing through a preheater (or heat exchanger) and then they are allowed to enter the converter. As they pass through the catalyst column, they ($\text{SO}_2 + \text{O}_2$) emerge as SO_3 . After the oxidation is initiated, no further heating is required as the reaction is exothermic and gases are allowed to go directly to the absorption tower.

(d) Absorption tower: Here the oxidized gases are absorbed by conc. H_2SO_4 when oleum is obtained. SO_3 is not absorbed in water. The strong

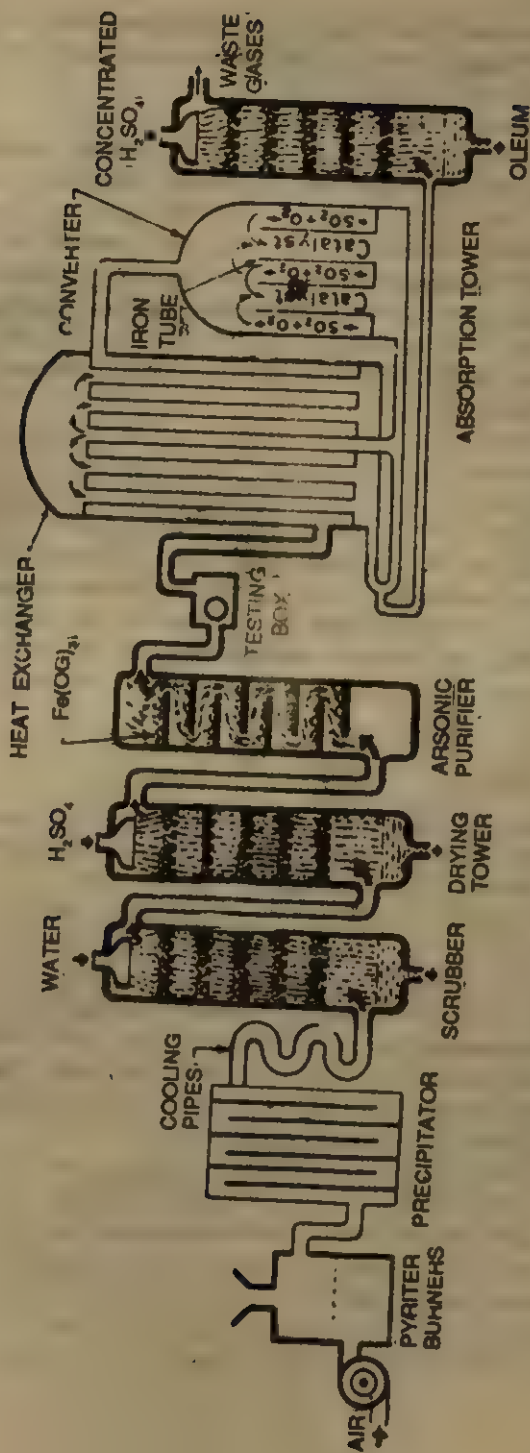


Fig. 13.16b An integrated diagram for the manufacture of sulphuric acid

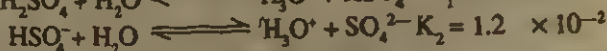
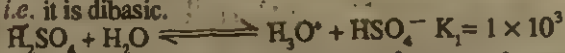
affinity of the gas for water causes a layer of fog particles to form about the bubbles as they pass through water. This prevents further dissolution of SO_3 . Hence, SO_3 is first absorbed in H_2SO_4 .

Properties and reactions of sulphuric acid

Pure sulphuric acid is a colourless oily liquid with a specific gravity of 1.84 at 288K (m.p. 283.5K; b.p. 593K). It fumes when heated due to decomposition of a small fraction of the acid into water and SO_3 . The high boiling point and viscous nature of the acid are due to the presence of partial hydrogen bonding (SO_4 groups are joined together by hydrogen bonds).

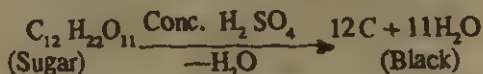
Concentrated H_2SO_4 (98%, 18M) dissolves in water with evolution of large amount of heat. The dilution is carried out safely by pouring acid slowly into water while the solution is stirred and cooled constantly to disturb the heat of dilution.

1. **Basicity.** The acid is a strong acid in aqueous solutions. It ionizes in two stages, i.e. it is dibasic.

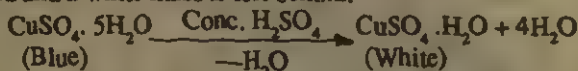


Two series of salts ($\text{M}^{2+} \text{SO}_4^{2-}$ and $\text{M}^+ \text{HSO}_4^-$) are, thus, possible.

2. **Dyhydrating properties:** Its strong affinity for water makes it a good dehydrating agent. Gases which do not react with the acid may be dried by passing through it. It removes water of crystallization from certain substances. It extracts water from cane sugar and leaves behind a black residual mass.



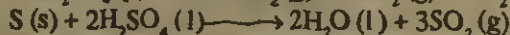
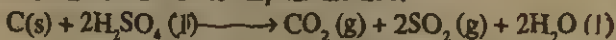
Similarly, crystals of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) lose four of its molecules of water of crystallization in the presence of concentrated sulphuric acid and a white mass is left behind.



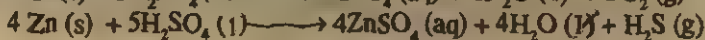
Dilute sulphuric acid does not have the dehydrating property.

3. **Oxidizing properties.** H_2SO_4 acts as an oxidizing agent, particularly when hot and concentrated. This property becomes weak on dilution.

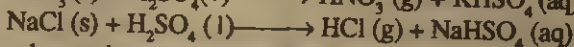
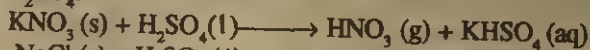
(i) **Action on non-metals.** In its reaction with non-metals, each molecule of H_2SO_4 provides one atom of nascent oxygen for oxidation purposes and is itself reduced to sulphur dioxide.



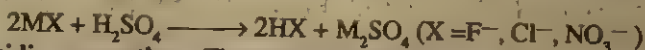
(ii) **Action on metals.** Depending upon the nature of metals, H_2SO_4 may undergo reduction to SO_2 , H_2S or S . Copper and zinc are oxidized to their sulphates by hot concentrated H_2SO_4 .



(iii) **Action on salts.** Concentrated H_2SO_4 reacts with certain salts forming acids and metal hydrogen sulphates. The acids produced so are not oxidized by H_2SO_4 .



Thus, it can be used to manufacture more volatile acids than H_2SO_4 from their salts.

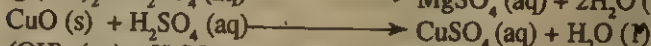
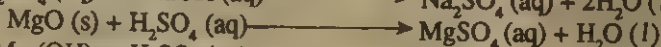
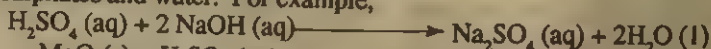


(iv) **Acidic properties:** The reactions of concentrated H_2SO_4 are often complex due to its oxidizing action, but dilute sulphuric acid behaves as a typical acid.

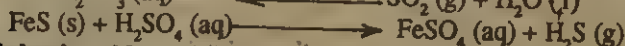
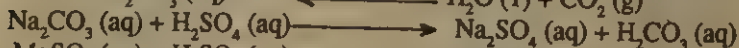
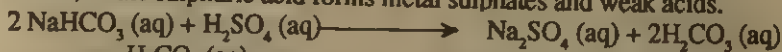
(i) **Reaction with metals above hydrogen in the electrochemical series:** Metals like Mg, Zn and iron reacts with dilute H_2SO_4 to form metal sulphates and H_2 gas.



(ii) **Reaction with bases and alkalis (metal oxides and hydroxides):** In its reaction with bases and alkalis, the acid neutralizes them and forms metal sulphates and water. For example,

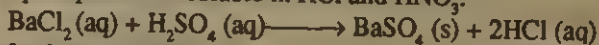


(iii) **Reaction with salts of weak acids:** In its reaction with salts of weak acids, dilute sulphuric acid forms metal sulphates and weak acids.



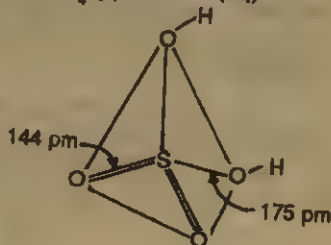
Test for sulphuric acid

A few mL of dilute sulphuric acid contained in a test tube is treated with a few drops of barium chloride solution. A white precipitate of BaSO_4 is formed. The precipitate is insoluble in HCl and HNO_3 .

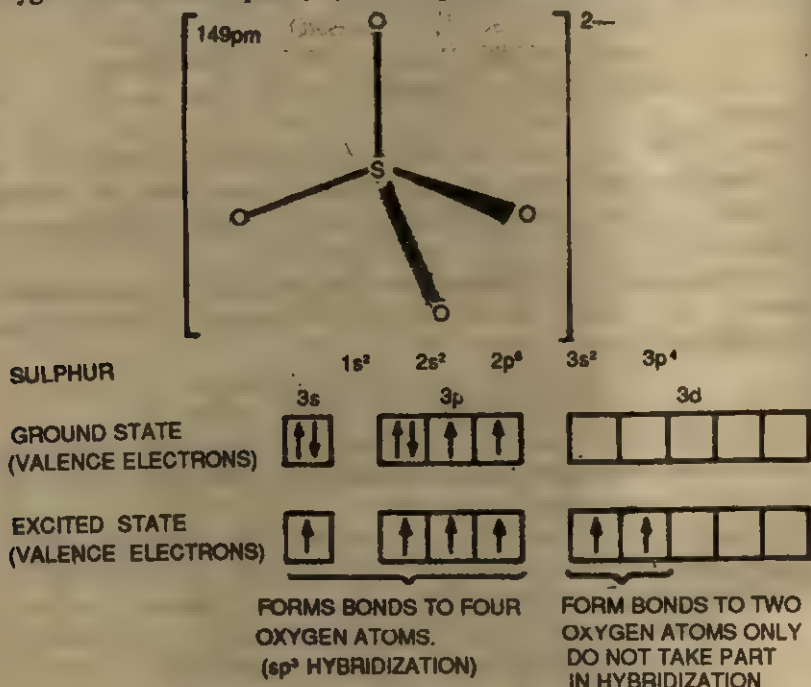


Structure of sulphuric acid

The structure of sulphuric acid in the vapour phase can be schematically portrayed as given here.

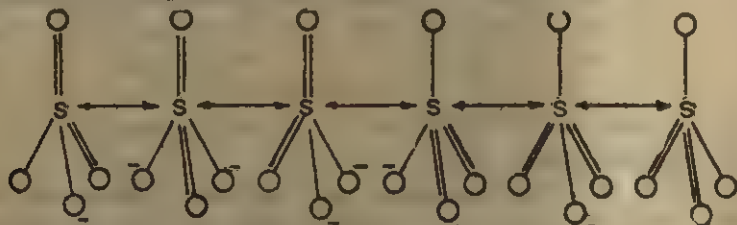


Sulphate ion adopts tetrahedral disposition of oxygen atoms around sulphur atom. The scheme of hybridization and the possible arrangement of oxygen atoms about sulphur (VI) atom is given below:



HYBRIDIZATION SCHEME FOR SULPHUR IN SO_4^{2-} ION

All the bond lengths are rather short (149 pm) because of resonance of the double bonds to give a resonance hybrid such as given below:



Resonance between equivalent canonical forms in SO_4^{2-}

Uses of sulphuric acid

Sulphuric acid is used in various types of industries. The consumption of H_2SO_4 is a measure of industrialization of a country. Chiefly it is used as given below:

1. In the manufacture of fertilizers (ammonium sulphate and super phosphate of lime), dyes, drugs, explosives (dynamite, TNT and picric acid) disinfectants, paints, pigments, plastics, textiles (cotton wool and linen fabrics) synthetic fibres (viscose rayon and acetate rayon) photographic

films, synthetic rubber, synthetic detergents and lacquers.

2. In the production of acids (HCl , HNO_3 , H_3PO_4 , etc.) diethyl ether, DDT, Na_2SO_4 , etc.

3. In the metallurgical operation of certain metals, e.g., copper etc., (extracted from their ores using H_2SO_4).

4. For the pickling of metal surfaces (removal of oxide layer from the surface of metals) before electroplating, galvanizing, soldering or enamelling.

5. In the refining of petroleum—sulphur, tarry compounds, etc., are removed by treating crude petroleum with H_2SO_4 .

6. As laboratory reagent, dehydrating and drying agent.

7. In storage batteries used in automobiles.

8. In pharmaceuticals and for making insecticides.

9. In leather tanning industries.

Acid rain

Rain water is usually acidic in nature because of the dissolution of the common pollutants, e.g., CO_2 , NO_2 , SO_2 , etc. present in the atmosphere. The atmosphere above the industrial area contains NO_2 and SO_2 and dust particles in abundance. Sulphur dioxide is produced from sulphur contaminants during the combustion of coal and heavy fuel oils, during the smelting of ores and in the production of sulphuric acid. Sulphur dioxide is oxidized to sulphur trioxide by the atmospheric air. This reaction is catalyzed by the particular pollutant, NO_2 or possibly may occur through a photoexcited state. SO_3 reacts with water present in the air to form H_2SO_4 . Nitrogen dioxide is obtained by the oxidation of nitrogen oxide by dioxygen and ozone present in the atmosphere. Nitrogen oxide, in turn, is generated from dinitrogen and dioxygen of the atmosphere in the high temperature regions, internal combustion engines, as well as in coal and oil burning furnaces. The tropospheric temperatures, decreasing with altitude permits warmer, less dense surface air to rise and carry away pollutants. Such pollutants dissolve in rain waters to make it highly acidic as vinegar. Acid rain can lead to extensive damage to marble monuments. It destroys the aquatic life. Aluminium compounds present in the soil react with acidic rain water and move away along with the stream of water into rivers, oceans and lakes etc. This causes poisoning of fishes. Acidic waters react with the essential macro and micro nutrients and kill the bacteria required for nitrogen fixation. All the resultant products move away along with the flowing water. Forests, the wealth of world, are also destroyed by the acid rain.

A variety of preventive measures are being taken to reduce the extent of atmospheric pollution. Sulphur containing compounds are successfully removed from most petroleum fuels during the refining process. Another method of preventing pollution is to trap pollutants by some mechanical device or to convert them to non-polluting substances. The electrostatic

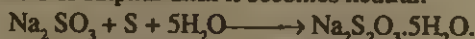
precipitators are being used to trap the pollutants but they are unable to trap gases like SO_2 etc. The simplest way is to blow powdered limestone into the source of SO_2 . Sulphur dioxide reacts with CaO from CaCO_3 and gets converted to CaSO_3 in the form of dust pollutant. Finally it is trapped. However, the long term effective planning of controlling the pollutants is to minimize the use of fossil fuels (coal and oil) by replacing them with smokeless sources of energy.

13.8.4 Sodium Thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

Commercially it is known as hypo. It is manufactured by passing sulphur dioxide through waste liquor of sodium sulphide containing other sodium salts of CO_3^{2-} , SO_3^{2-} and SO_4^{2-} . $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ crystallizes out on allowing the solution to stand. A small amount of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ crystals is also added as it makes the solution supersaturated.

Some other methods employed in the preparation of hypo are as follows:

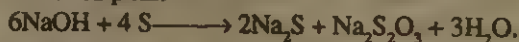
(i) **From sodium sulphite:** A concentrated solution of sodium sulphite is boiled with flowers of sulphur until it becomes neutral.



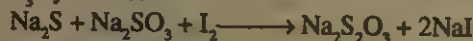
The excess of sulphur is filtered off and the filtrate is concentrated by evaporation to get the crystals of sodium thiosulphate.

This method is also used to get the salt on a commercial scale.

(ii) **From caustic alkali.** In this method, sodium hydroxide solution is boiled with flowers of sulphur.

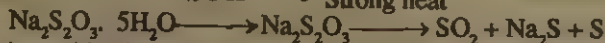
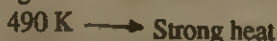


(iii) **From Springer's reaction.** It involves the oxidation of a mixture of Na_2S and Na_2SO_3 by iodine.

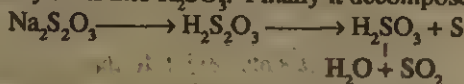


Properties of sodium thiosulphate

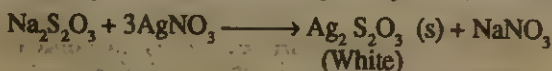
Sodium thiosulphate (m.p. 321K) is a white crystalline of efflorescent solid. On heating upto 490K it loses water and finally the anhydrous salt decomposes on strong heating.



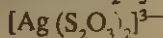
On treating with dilute HCl it gives $\text{H}_2\text{S}_2\text{O}_3$, which on keeping loses sulphur and gradually turns into H_2SO_3 . Finally it decomposes giving SO_2 .



Its aqueous solution reacts with silver nitrate solution to give a white precipitate of $\text{Ag}_2\text{S}_2\text{O}_3$ which quickly changes to yellow, brown and finally black Ag_2S .



This test is employed for the detection of $\text{S}_2\text{O}_3^{2-}$ ions. In excess of $\text{S}_2\text{O}_3^{2-}$ solutions, $\text{Ag}_2\text{S}_2\text{O}_3$ dissolves forming thiosulphate



and $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$

Sodium thiosulphate also dissolves AgCl and AgBr completely due to the formation of complexes.

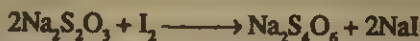


This reaction is used in photography for fixing.

It acts as a reducing agent. On reacting with Cl_2 it gets oxidized to HSO_4^-



This reaction is the basis of its use as 'antichlorine' in textile industry. Iodine oxidizes it to tetrathionate $\text{S}_4\text{O}_6^{2-}$ ions. ($\text{S}_2\text{O}_3^{2-}$ decolourizes I_2 solution).

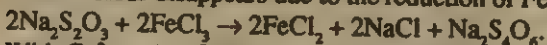


The reaction with iodine is the basis of iodometric titrations in volumetric analysis.

Metallic ions Cu^{2+} , Fe^{3+} or Au^{3+} oxidize thiosulphate solution to tetrathionate.



Violet colour disappears due to the reduction of Fe^{3+} ions.



With Cu^{2+} and Au^{3+} salt solutions, thiosulphate forms complexes with the reduced ions Cu^+ and Au^+ - forming $[\text{Cu}(\text{S}_2\text{O}_3)_2]^{3-}$ and $[\text{Au}(\text{S}_2\text{O}_3)_2]^-$. Hydrogen peroxide and acidified KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ oxidize it to sulphate.

Uses of sodium thiosulphate

It is used: (i) in photography as a fixer and developer, (ii) in the extraction of gold and silver from their ores, (iii) as an antichlorine to remove chlorine from bleached articles, (iv) in medicine, and (v) as a laboratory reagent.

13.9 HALOGENS

Fluorine (F), chlorine (Cl), bromine (Br) and iodine (I) are collectively known as halogens. The name halogen is derived from the Greek word 'halos' which means 'sea salt former'. This reflects that most of these elements exist in sea water in the form of salts. These elements constitute group 17 of the periodic table. Astatine, the last element in this group is radioactive. Its properties seem to follow the trend in the halogen family. Little is known about astatine due to its radioactive nature and short half-life. The longest lived nuclide is ^{210}At with a half-life of 8hr.

Family relationship and general trends

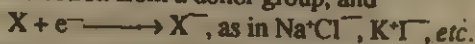
All halogens exist as diatomic molecules at ordinary conditions. The molecules are held together by van der Waals forces (weak forces). The strength of these forces increases with increasing size of molecules. Thus, the physical state of these elements changes from gas to liquid to solid (Table 13.5). Because of the increasing van der Waals forces, the melting and boiling points of the halogens increase from fluorine to iodine.

They are all coloured because they absorb light in the visible region

resulting in the excitation of outer electrons to higher energy levels. The smaller the atom, more will be the energy needed for excitation. Gaseous F_2 molecules absorb high energy violet light and appear greenish yellow while gaseous I_2 molecules absorb low energy yellow light and appear violet. Similarly chlorine molecules appear greenish-yellow and bromine molecules reddish brown (Table 13.5).

The members of the family are very similar in chemical behaviour. Since they have seven electrons in the valence shell, ns^2np^5 . They have only one electron less than the number present in the adjacent noble gas. They can acquire a noble gas electronic configuration by:

- (i) accepting one electron from a donor group, and



(halogen atoms become stable univalent ions)

- (ii) forming a single covalent bond as in the halogen molecules ($X - X$) and hydrogen halides ($H - X$).

TABLE 13.5. Atomic and molecular properties of halogens

Property	F	Cl	Br	I
Atomic number	9	17	35	53
Electron structure	$[He]2s^22p^5$	$[Ne]3s^23p^5$	$[Ar]3d^{10}4s^24p^5$	$[Xe]4d^{10}5s^25p^5$
Covalent radius (pm)	72	99	114	133
Ionic radius (pm)	136	181	195	216
Electron affinity ($kJ\ mol^{-1}$)	333	349	325	296
Ionization potential ($kJ\ mol^{-1}$)	1681	1255	1142	1007
Electron egativity	4.0	3.0	2.8	2.5
Oxidation states	-1	-1, +1, +3, +5, +7,	-1, +1, -3, +5, +7,	-1, +1, -3, +5, +7
	F_2	Cl_2	Br_2	I_2
Melting point (K)	53	172	266	306
Boiling point (K)	85	238	332	456
Density g/cm^3	1.1	1.5	3.2	4.9
Physical State	Gas	Gas	Liquid	Solid
Colour	8 Yellow	Greenish Yellow	Reddish Brown	Greyish Black
Bond distance (pm)	143	199	228	266
Bond dissociation energy ($kJ\ mol^{-1}$)	159	243	193	151
Heat of vapourization, ΔH_{vap} ($kJ\ mol^{-1}$)	3.347	9.204	15.99	31.18
Electrode potential E° (V)	+2.85	+1.36	+1.07	+0.55
$X_2 + 2e^- \rightarrow 2X^-$			Br (l)	I(s)

The lower value of electron affinity for fluorine appears to be the consequence of electron-electron repulsions within the small and highly dense electron cloud of the fluorine atom. The decrease in electron affinity values from chlorine to iodine depicts the low tendency of atoms to gain electrons.

The heats of dissociation (bond energy) decrease regularly from chlorine to iodine, indicating a decrease in molecular stability. The reason for the comparatively low value of bond energy for fluorine ($F-F$) is probably due to strong repulsion between non-bonding electrons on the two atoms in F_2 . A consequence of this weak bond is that fluorine is more reactive than the other halogens. The heats of vapourization increase from fluorine to iodine but all values are small in magnitude, depicting weak forces of the van der Waals type between the molecules in the solid state (molecules are arranged in layer).

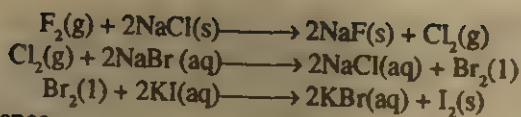
The data in Table 13.5 show that halogens are typical molecular substances. They all have low m.p. and b.p. values and all are non-conducting. Iodine and bromine are much more dense than chlorine and fluorine. This is because of the difference in their physical states.

All the halogens show -1 oxidation state. Except fluorine, rest of the halogens exhibit $+1$, $+3$, $+5$ and $+7$ oxidation states. Fluorine is the most electronegative of all the halogens. It shows only -1 oxidation state. The other halogens show $+1$ oxidation state in interhalogen compounds like, ClF , BrF , ICl . Fluorine does not exhibit higher oxidation states as there is no possibility of expanding the valence shell to contain more than eight electrons. The other halogens have vacant d orbitals in the valence shell which can be used in bonding. For example, a pair of electrons in a p orbital may be promoted to a vacant d orbital. Similarly by the involvement of remaining two pairs of electrons in the valence shell higher oxidation states can be achieved. The energy necessary for splitting up the electron pairs and promoting electrons to higher energy levels is obtained from the energy released when covalent bond formation occurs.

The abnormally high electrode potential values (decreasing from fluorine to iodine) show high reactivity in solution. Thus, each halogen is the most reactive non-metal of its period.

The halogens are extremely active elements because of their strong tendency to gain one or more electrons. However, there is a regular decrease in chemical activity from fluorine to iodine, $F_2 > Cl_2 > Br_2 > I_2$. Fluorine is the most reactive of all the non-metals.

Halogens are excellent oxidizing agents. Fluorine is the most electronegative element, i.e., the strongest electron acceptor, and therefore, is the strongest oxidizing agent. The oxidizing action of the halogens decreases in the order, $F > Cl > Br > I$. The relative oxidizing power is well evident in the displacement reactions.



13.9.1 Occurrence

Halogens do not occur free in nature due to their highly reactive nature. They are generally found in combination with metals as simple halides. Table 13.6 shows the relative abundance of the halogens in nature.

TABLE 13.6 Abundance of halogens in nature

Element	Abundance in earth's Crust (ppm)	Abundance in sea water (ppm)
Fluorine	800	8
Chlorine	400	19000
Bromine	2	65
Iodine	0.3	Extremely small

The most reactive fluorine is found in the combined form as fluoride in rocks and in many natural water supplies. Fluorine occurs in a number of minerals, the most common being fluorspar, CaF_2 ; cryolite, Na_3AlF_6 ; and fluorapatite, $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$.

Chlorine is mainly found as sodium chloride, NaCl in sea water. It is also present in sea water with other alkali and alkaline earth chlorides. Brine wells and rock salt (NaCl) deposits make a rich source of chlorine.

Bromine is also found in sea water as bromides (NaBr , KBr , MgBr_2). It is also found in salt mines as sodium bromide.

Sea water is a poor source of Iodine. However, seaweeds absorb some iodides from sea water and make a good source for iodine. Chile has extensive deposits of calcium iodate which is found along with the deposits of sodium nitrate.

13.9.2 Preparation of Halogens

Fluorine:

Difficulties in the Isolation of Fluorine :

Fluorine is highly reactive. Its reactivity resisted the efforts of chemists to isolate it for quite long even though its compounds were plentiful. Its toxic nature proved to be hazardous for the chemists. Fluorine appeared to be so powerful that no vessel could resist its chemical action until platinum vessels were utilised. Later vessels made of copper or monel metal (Cu-Ni-Fe alloy) were used. These vessels are found to be attacked initially but metal fluoride produced during the reaction soon forms a protective coating preventing further action.

Usual methods of oxidizing the halide ions to the elemental halogens are not employed as there is no other substance that can oxidize fluoride ions to fluorine. Fluorine itself is the most powerful oxidizing agent of all the

elements. This is quite evident from the high reduction potential for fluorine (Table 13.5).

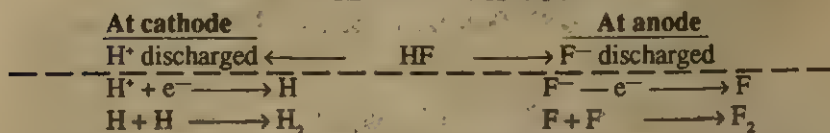
The preparation of the pure fluorine is quite difficult due to its high reactivity and its strong affinity for hydrogen. Early attempts to isolate fluorine using electrolytic methods failed because electrolysis of aqueous solutions of hydrogen fluoride yielded oxygen and the anhydrous acid is a non-conductor.

Gaseous fluorine is normally prepared by electrolysis of perfectly dry molten mixture of approximate composition of KHF_2 and HF at 373K using hard carbon anode and steel cathode. Originally graphite electrodes were used. Graphite was found unsuitable for the anode as it was slowly corroded forming compounds [lamellar compound $(\text{CF})_n$]. It increases the electrical resistance, and thus, requires more current. As a result, the cell gets heated up, and eventually, an explosion takes place. To prevent explosion, carbon mixed with copper is used as the anode.

The fluorine produced generally remains mixed up with HF which may be removed regularly by passing the gas over solid sodium fluoride.



The temperature of the cell is maintained at 373K. Since hydrogen and fluorine combine explosively, mixing of fluorine with hydrogen is always avoided. A diaphragm made of teflon is used to separate the cathode and anode. KHF_2 decomposes as given below:



Various types of the cells have been developed from time to time. It will not be out of place to make a mention of the apparatus used by Moissan (1886) along with the other cells.

In Moissan's apparatus (Fig. 13.17) both the vessel and the electrodes of Platinum-iridium were used. The open ends of the tube were closed with fluorspar stoppers through which electrodes passed into U-tube. During the reaction the apparatus was suspended in a bath of evaporating methyl chloride (250K) to avoid the evaporation of anhydrous HF . Dennis, Veeder and Rochow (1931) improved upon the Moissan's tube by using copper cell fitted with graphite electrodes. This cell is called Dennis' cell. There is another cell called Whytlaw Gray's cell. This cell is employed for producing fluorine on the commercial scale also. In industry, a mild steel pot is used as the cathode. A carbon rod free from graphite is used as the anode. In Whytlaw Gray's cell electrolysis of fused KHF_2 in HF is done in an electrically heated copper (or steel) vessel which serves as cathode also.

Anode made of copper mixed with graphite is used. It is enclosed in a copper (or steel) diaphragm perforated at the bottom. This diaphragm avoids the mixing of H_2 and F_2 . Hydrogen and fluorine are collected at their respective electrodes.

This method is far superior than the Moissan's method. Chances of fluorine mixing with hydrogen have been avoided by using diaphragm. Wide openings are provided for the smooth escape of gases, and thus, frothing of the electrolyte is reduced. The apparatus employed is shown in Fig. 13.18. The fluorine obtained is quite pure and is compressed in steel cylinders.

Chlorine

Chlorine is prepared commercially by electrolysis of natural brines or concentrated aqueous sodium chloride. Industrially important hydrogen and caustic soda are also obtained as by products.

A large number of electrolytic cells have been developed. However, the commonly used is Nelson's cell (Fig. 13.19).

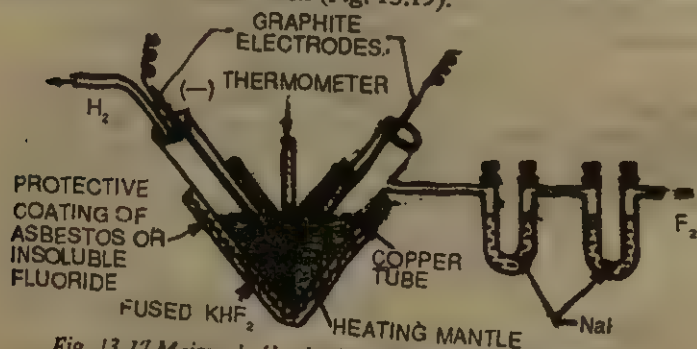


Fig. 13.17 Moissan's U-tube for the preparation of fluorine

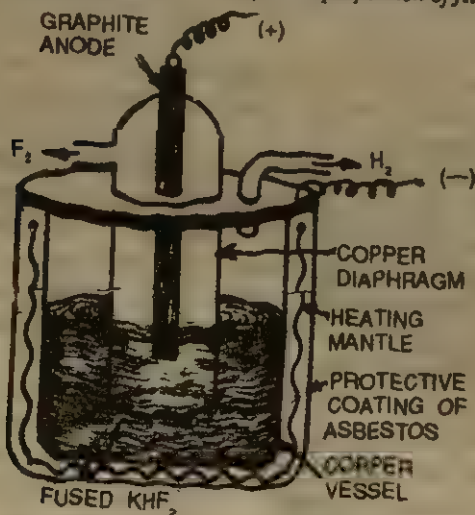
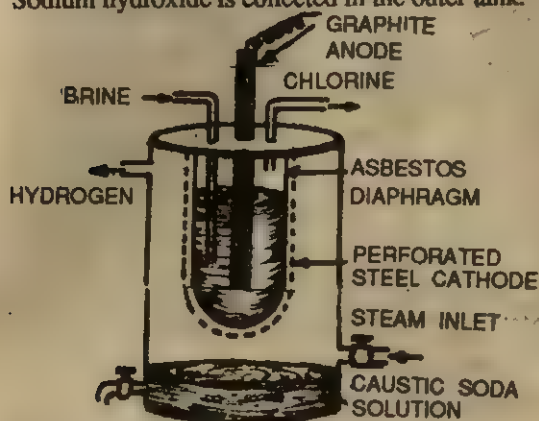


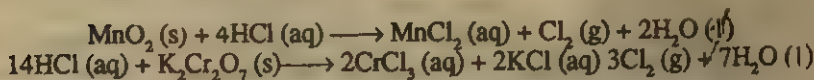
Fig. 13.18 Whytlaw Gray's cell for the preparation of fluorine.

When electric current is passed through the cell, chlorine is liberated at the anode and is allowed to escape through the outlet. The chlorine gas is compressed into steel cylinders. On the other hand Na^+ ions start moving towards the cathode through the asbestos paper. Before they could reach the cathode, there already occurs reduction of water, liberating OH^- ions and hydrogen. The Na^+ ions combine with OH^- ions to form NaOH . The hydrogen gas is drawn off through the exit at the top and collected as such. Sodium hydroxide is collected in the outer tank.

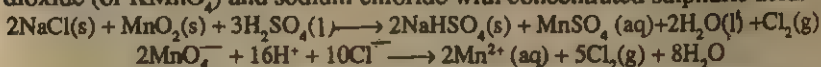


Laboratory methods for the preparation of chlorine involve oxidation of hydrochloric acid with manganese oxide, MnO_2 , or potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$.

Fig. 13.19 Nelson cell



Chlorine can also be prepared by gently heating a mixture of manganese dioxide (or KMnO_4) and sodium chloride with concentrated sulphuric acid.



Powdered manganese dioxide is put in a round bottom flask and concentrated sulphuric acid is added through a thistle funnel. On heating the contents, effervescence takes place and a greenish-yellow chlorine gas is produced. The chlorine gas is then dried by bubbling through concentrated sulphuric acid and is collected by upward displacement of air.

The assembly used for the preparation of chlorine from sodium chloride is shown in Fig. 13.20.

Bromine

The methods for laboratory preparation of bromine are similar to those for chlorine. Accordingly bromine can be prepared by heating a mixture of KBr and manganese dioxide with concentrated H_2SO_4 .



In addition, bromine may be produced by the oxidation of the bromide ion by chlorine. Chlorine being more electronegative than bromine attracts

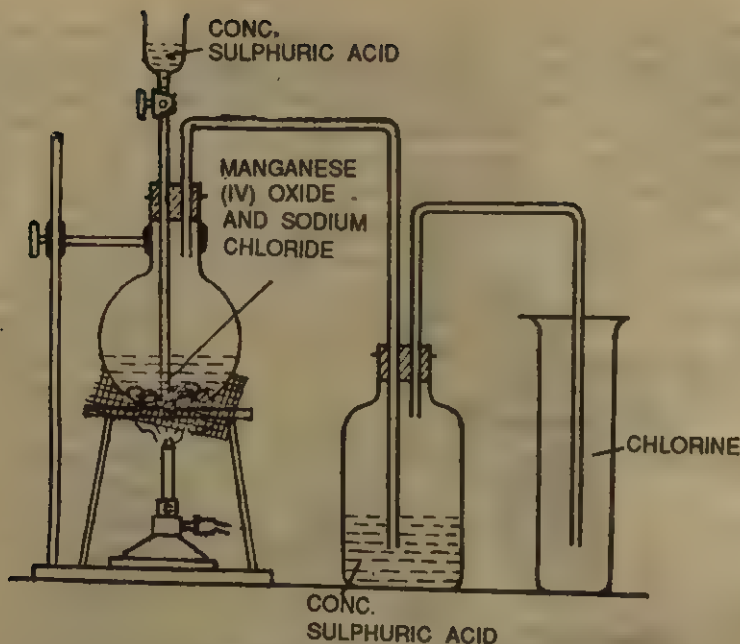
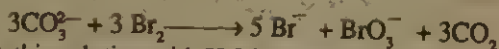


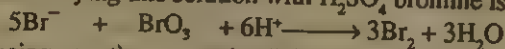
Fig. 13.20 Preparation of chlorine from sodium chloride

an electron from bromide ion; thereby oxidizing the bromide ion to free bromine. $2\text{Br}^-(\text{aq}) + \text{Cl}_2(\text{g}) \longrightarrow \text{Br}_2(\text{g}) + 2\text{Cl}^-(\text{aq})$

This principle is also used in the commercial production of bromine from sea water (contains as Br^-). The bromine, thus, produced is blown out of the solution by a stream of air which, in turn, is passed through an aqueous solution of sodium carbonate; sodium bromide and sodium bromate are formed.



On acidifying this solution with H_2SO_4 bromine is obtained.

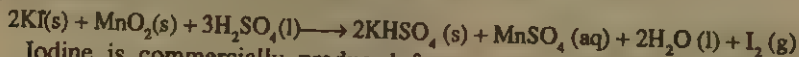


(reducing agent)

(oxidizing agent)

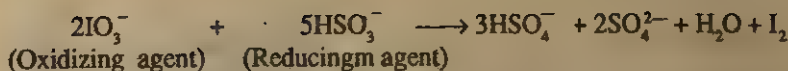
Iodine

Iodine can be prepared in the laboratory by using potassium iodide in place of KBr.



Iodine is commercially produced from sea weeds which concentrate iodide ion from sea water. Combustion of sea weeds produces iodide ion which, in turn, can be oxidized by chlorine gas in a manner similar to that described for the production of bromine.

Iodine occurs in the form of sodium iodate, NaIO_3 , in crude Chile salt petre, NaNO_3 . The iodine is obtained by reducing the iodate with sodium hydrogen sulphite:



Chemical reactions of halogens

Halogens undergo a variety of chemical reactions. The reactivity decreases in the order $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$. Some of these are summarized in Table 13.7.

All halogens react with water at different rates. Fluorine reacts vigorously and instantaneously with water to give HF and some other products, e.g., OF_2 . HOF has been characterized and isolated by fluorinating ice at 233K. This acid is highly unstable and decomposes to give HF and O_2 . Molecular fluorine is the strongest chemical oxidant known, under all conditions.

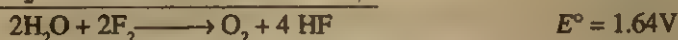


TABLE 13.7. Some chemical properties of halogens

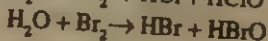
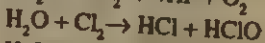
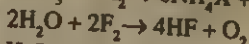
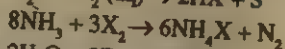
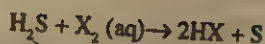
S. No.	Reaction with	Reaction equation	Remarks/conditions
1.	Metals		
	(a) Active metals (Na, Mg)	$2\text{Na} + \text{X}_2 \rightarrow 2\text{NaX}$ $\text{Mg} + \text{X}_2 \rightarrow \text{MgX}_2$	$\text{X} = \text{F, Cl, Br, I}$
	(b) Less active metals (Fe, Al)	$2\text{Fe} + 3\text{X}_2 \rightarrow 2\text{FeX}_3$ $2\text{Al} + 3\text{X}_2 \rightarrow 2\text{AlX}_3$	$\text{X} = \text{F, Cl, Br, I}$
2.	Non-Metals (P)	$\text{P}_4 + 6\text{X}_2 \rightarrow 4\text{PX}_3$ $\text{P}_4 + 10\text{Cl}_2 \rightarrow 4\text{PCl}_5$	$\text{X} = \text{F, Cl, Br, I}$
3.	Hydrogen	$\text{H}_2 + \text{F}_2 \rightarrow 2\text{HF}$ $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$	Reaction explosive even at low temp. and in dark. Reaction slow in dark. Fast in sunlight. Reaction only in presence of Pt catalyst at 473K. Reaction incomplete even in presence of Pt catalyst.
4.	Alkali (NaOH)	$2\text{NaOH} + \text{X}_2 \rightarrow \text{NaX} + \text{NaOX} + \text{H}_2\text{O}$ (cold dil.) $6\text{NaOH} + 3\text{X}_2 \rightarrow \text{NaXO}_3 + 5\text{NaX} + 3\text{H}_2\text{O}$ (hot conc.) $2\text{NaOH} + 2\text{F}_2 \rightarrow 2\text{NaF} + \text{OF}_2 + \text{H}_2\text{O}$ (cold dil.) $4\text{NaOH} + 2\text{F}_2 \rightarrow 4\text{NaF} + \text{O}_2 + 2\text{H}_2\text{O}$ (conc. hot)	$\text{X} = \text{Cl, Br, I}$

5. Oxidizing character

(a) H_2S

(b) NH_3

(c) H_2O



Oxidizing action decreases in the order $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.

$\text{X} = \text{Cl}, \text{Br}, \text{I}$

$\text{X} = \text{Cl}, \text{Br}$

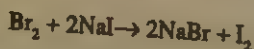
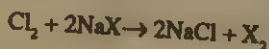
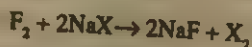
Vigorous reaction

Rapid reaction

Slow reaction

No reaction with I_2 .

6. Displacement reactions



$\text{X} = \text{Cl}, \text{Br}, \text{I}$, F_2 displaces all other halogens from their halides.

$\text{X} = \text{Br}, \text{I}$, Cl_2 displaces

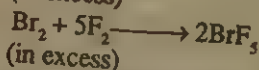
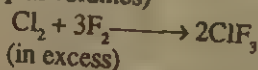
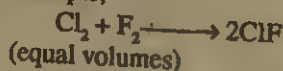
Br_2 and I_2 .

Br_2 displaces I_2 . I_2 does not displace any other halogen.

13.10. COMPOUNDS OF HALOGENS

13.10.1 Interhalogen compounds

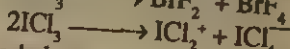
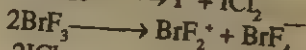
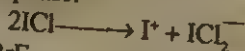
Each halogen reacts with every other halogens to form compounds known as interhalogen compounds, XX_n where $n = 1, 3, 5$ or 7 . Their formation is ascribed to the small electronegative difference between the two halogen atoms. These can be prepared by direct combination of molecular halogens. For example,



Interhalogens are highly reactive substances. Their reactivity is better than the parent halogens (except fluorine) because their dissociation energy is less than halogens. The stability of these compounds increases as the size of the central atom increases. They are covalent liquids or gases. They are good oxidizing agents and are hydrolysed easily. ClF_3 is an excellent fluorinating agent. Some of the compounds react with alkali metal halides and give polyhalides. e.g. BrF_4^- .



Conductivity measurement depicts a tendency of self-ionization among some interhalogens in liquid phase.



Some of the known interhalogens are listed in Table 13.8.

TABLE 13.8. Interhalogen compounds

Name	AX	AX ₃	AX ₅	AX ₇
Fluorides	ClF (g)	ClF ₃ (l)	ClF ₅ (l)	—
	BrF (l)	BrF ₃ (l)	BrF ₅ (l)	IF ₇ (g)
	IF (g)	IF ₃ (l)	IF ₅ (l)	—
Chlorides	BrCl (g)	ICl ₃ (s)	—	—
	ICl (s)	(I ₂ Cl ₆)	—	—
Bromides	IBr (s)	—	—	—

On the basis of VSEPR theory (Unit 6) and taking into account the lobes with unshared pair of electrons and bond pairs, the possible geometry of some of the interhalogens and polyhalide ions are illustrated through Fig. 13.21.

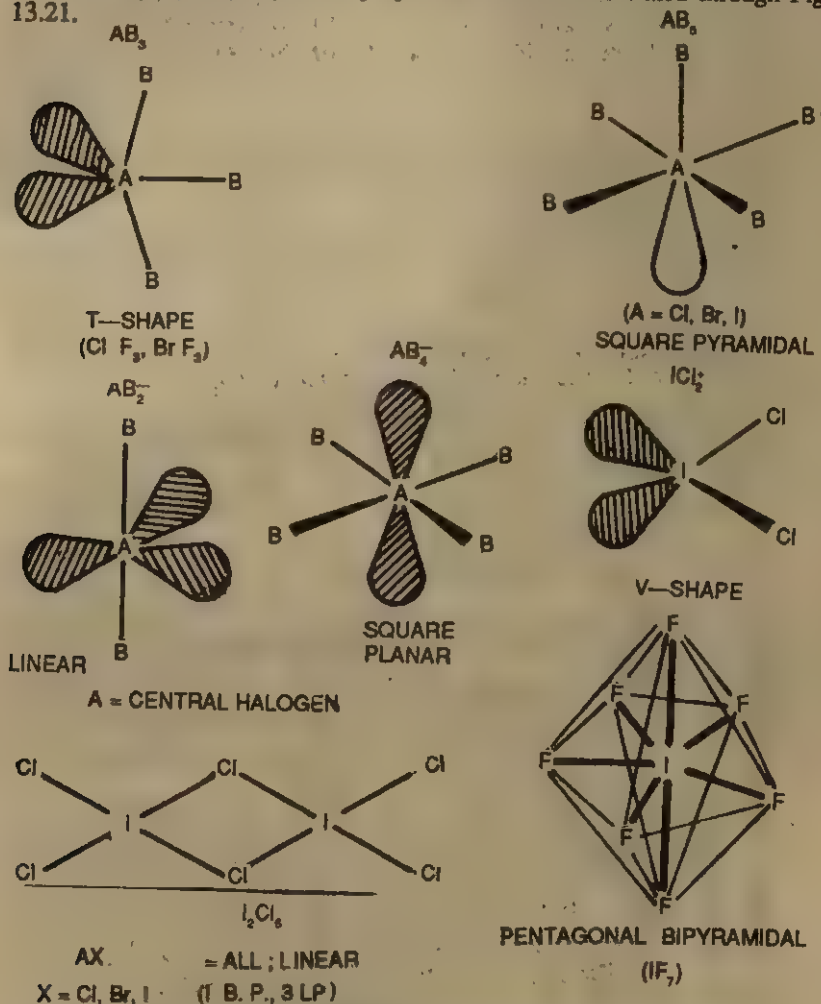


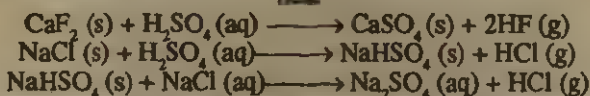
Fig. 13.21 Geometry of some interhalogen compounds and polyhalide ions.

13.10.2. Hydrogen halides (hydrides)

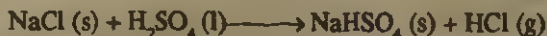
All the halogens react with dihydrogen and form volatile hydrides of the general formula, HX .

Various methods are used for the preparation of hydrides of halogens. Binary hydrides of halogens can be prepared by the direct union of their constituent elements under appropriate conditions.

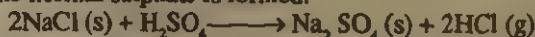
Commercially hydrogen fluoride and hydrogen chloride are produced by heating fluoride and chloride (aq) with concentrated sulphuric acid.



These methods are also employed for the laboratory preparation of HF and HCl . Hydrogen chloride is more volatile than sulphuric acid and is removed from the reaction as it is formed, thereby driving the reaction to completion.



Only at higher temperatures than those normally attained in the laboratory, the normal sulphate is formed.



The gas is collected by upward displacement of air as the gas is heavier than air (Fig. 13.22). Hydrogen chloride is dried by bubbling through concentrated sulphuric acid.

On a large scale, hydrogen chloride can be produced by burning chlorine in hydrogen. A large amount of hydrogen chloride is available as a by product in the chlorination of organic compounds.

The HF and HCl , thus, produced are absorbed in water forming hydrofluoric and hydrochloric acids.

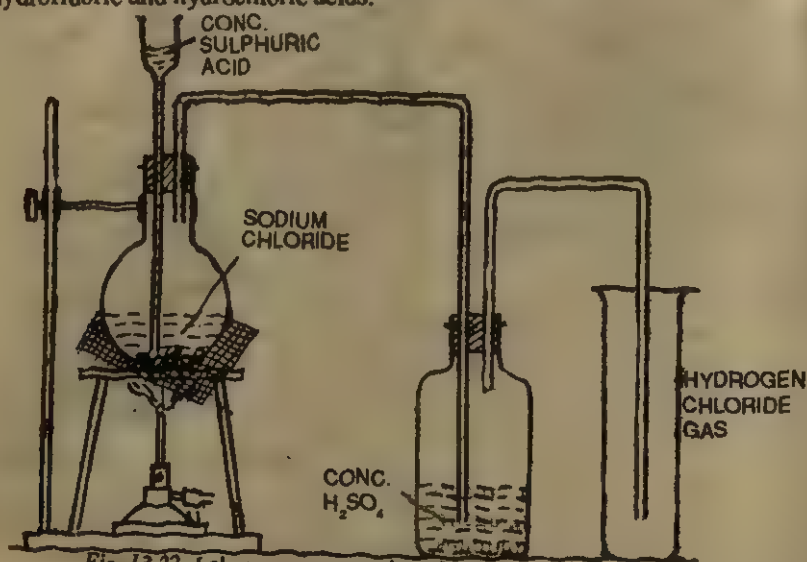
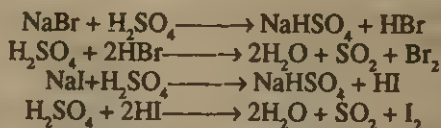


Fig. 13.22 Laboratory preparation of hydrogen chloride gas.

In the preparation of HBr and HI, this method gives rise to certain undesirable products, hence, is not used. Both HBr and HI are oxidized by H_2SO_4 .



Hydrogen halides can also be prepared by the hydrolysis of covalent halides of certain non-metals. PCl_3 , PBr_3 , PI_3 and SCl_4 generally react with water to form two acids—the HX and an oxyacid of the non-metal other than halogen.

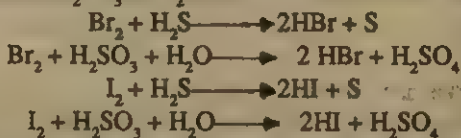


This method is commonly employed for the preparation of HBr and HI. Pure HF can be prepared by heating potassium hydrogen fluoride.



Hydrogen fluoride is also a by product of the phosphoric acid industry but the presence of SiO_2 leads to the formation of H_2SiF_6 from which it is not easy to recover HF profitably.

Aqueous HBr and HI can be prepared by the reduction of the molecular halogen by means of H_2SO_3 or H_2S .



Properties: At room temperature all the hydrogen halides are colourless gases with an irritating odour. Like the elements, the binary hydrides show similarities and regular trends in properties in order of increasing atomic number. They show no acid character when perfectly dry. In solution, HCl, HBr and HI are strong acids but HF is relatively weak (ionizes only 5 %). This can be ascribed to strong electronegative nature of fluorine which makes its compounds highly stable. They are all polar covalent compounds. The polarity is maximum for HF and minimum for HI.

At ordinary temperatures, HF molecules polymerize through hydrogen bonding Fig. 13. 23.

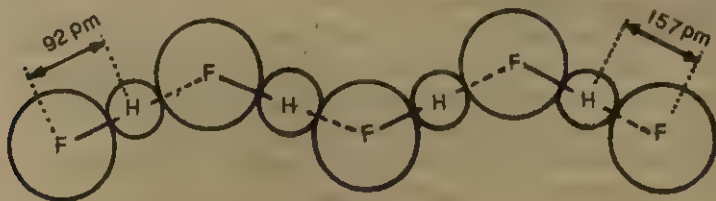


Fig. 13. 23. Polymeric molecule of hydrogen fluoride resulting from hydrogen bonding.

TABLE 13.9 Some physical properties of binary hydrides

Property	HF	HCl	HBr	HI
Physical state at 288K	Liquid	Gas	Gas	Gas
Melting point (K)	190	158.4	186	222
Boiling point (K)	292.5	189	206	238
Heat of formation ΔH_f (kJ mol ⁻¹)	-270.9	-92.4	-30.67	-5.55
Bond energy (kJ mol ⁻¹)	566	431	366	299
$\text{HX (g)} \rightarrow \text{H (g)} + \text{X (g)}$				
Bond length (pm)	86	128	142	160
Heat of vapourization, ΔH_{vap} (kJ mol ⁻¹)	7.77	16.21	17.68	19.8
Dipole moment (Debye)	1.98	1.03	0.78	0.38
Percentage ionic bonding	43	17	12	5
Solubility in water g/100g of water at 273 K	∞	82.3	221	234 at 283K

Binary hydrides decompose when heated sufficiently. HI decomposes most easily while HF and HCl show only minor dissociation even at 1273K. Thus, their thermal stability decreases as the formula weight increases. They fume in moist air and are soluble in water. In anhydrous state they are almost chemically inactive and do not attack metals at ordinary temperatures.

Binary hydrides are covalent substances, But their aqueous solutions conduct electricity. On dissolving the hydrides, the H — X bond is broken and the proton becomes hydrated.



The heat of formation of H_3O^+ ion initiates the dissociation of bond. Since the bond in HI is the weakest, it ionizes strongly in solution. Thus, acid strength decreases in the order $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$. Salts of these acids are called halides, the most important of which is NaCl.

Values of heats of formation and dissociation show a decrease in bond strength from HF to HI.

Of the four hydrides, HI is the most reducing agent. I^- is the most powerful electron donor. The reducing power of the hydrogen halides follows the sequence $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.

HF has no reducing properties. The highest b.p., heat of formation and the bond energy and the lowest heat of vapourization for HF compared to other hydrides are ascribed to hydrogen bonding present in HF molecules.

13.10.3 Uses of halogens and their compounds

Halogens and their compounds have found various applications. Some of their applications are summarized in Table 13.10.

TABLE 13.10 Major applications of halogens and their compounds

Halogens	Areas of application
Fluorine	<p>Both fluorine and HF in the preparation of fluorocarbons (Section 10.9), UF_6 (used in the separation of isotopes of uranium), SnF_2 (effective in preventing tooth decay) and NaF (an insecticide, a salt used in fluoridation of drinking water, as a flux and as a fungicide on wood).</p> <p>Fluorine as an oxidizing agent in rockets.</p> <p>HF in the preparation of cryolite, Na_3AlF_6 (used in the metallurgy of Al), BF_3 (serves as a catalyst in the industrial manufacture of certain organic compounds), CaF_2, etc., (used as a flux). Used in etching glass (manufacture of graduated glass wares, thermometres, etc.). ClF_3 and BrF_3 as fluorinating agents.</p> <p>Fluorine as a strong oxidizing agent.</p>
Chlorine	<p>Chlorine as a germicide and disinfectant in the purification of water; in the manufacture of plastics (PVC), synthetic rubbers, antiseptics and insecticides (DDT), dyes, drugs and chlorine containing solvents (used in dry cleaning), in metallurgical operations, e.g., recovering of gold, etc.; in industries for the preparation of chemicals, e.g., HCl, chloroform, bleaching powder (germicide, deodourizer), $NaClO$ (bleaching agent), chlorates and perchlorates (used in matches, fireworks and explosives), poisonous gases (phosgene, tear gas and mustard gas) etc. Chlorine water as an external antiseptic; as a strong bleaching agent for fabrics. HCl in the manufacture of metal chlorides, dyes, glue, glucose, etc.; in removing oxide coatings from iron or steel.</p>
Bromine	<p>Bromine in the manufacture of ethylene dibromide (a constituent of antiknock gasoline alongwith lead tetraethyl), dyes, AgBr (for photographic emulsions), bromides of sodium and potassium (in medicines as sedatives and soporifics), drugs, methyl bromide (as fire extinguishers) and organic compounds (xylyl bromide or bromoacetone as tear gases).</p> <p>Bromine as an oxidizing agent. BrF_3 as a strong fluorinating agent.</p>
Iodine	<p>Iodine in the manufacture/preparation of tincture of iodine (iodine in alcohol along with KI acts as an antiseptic), dyes, AgI (for photographic emulsions), KI or NaI (used in medicine for the treatment of goitre and other thyroid disorders), pharmaceutical chemicals, organic compounds—iodoform, indole (antiseptic) and polaroid.</p> <p>Iodine as a disinfectant, a reagent in laboratories and an organic catalyst.</p>

13.11 NOBLE GASES

The atmosphere contains a family of gaseous elements, the noble gases,

which remained undiscovered on the earth until 1894. These gaseous elements, helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) constitute the group of the periodic table. Radon, the last member of the family is not present in the atmosphere.

These gases are collectively known by different names, rare gases, inert gases or noble gases. The term inert is no longer applicable to the group as a whole because the heavier three members of the family (particularly xenon) are not inert. It is best to call them noble gases which would mean rightly their reluctance to react. You might recall at this moment the usage of the term noble to describe the chemistry of some metals such as gold, platinum, etc. Because of their low abundance on the earth, they have also been called rare gases.

All noble gases, except helium, have the stable outer electronic configurations ns^2np^6 . Helium has the $1s^2$ configuration. The stable electronic configuration well explains their high degree of chemical inertness in common chemical reactions. This configuration is also associated with inertness of ionized elements, e.g., Na^+ , Ca^{2+} , Al^{3+} , etc., and is the basis of the 'octet rule'.

The unique chemical inertness associated with the name of the noble gases is reflected in the history of their discovery which was followed by a long gap of a few decades before xenon could be made to combine with only the most electronegative element fluorine.

13.11.1 Discovery of the noble gases

The existence of these elements was not foreseen by Mendeleev. The story of the discovery and investigation of the noble gases is one of the most brilliant and interesting topics in the History of Science. This can be traced back to 1785 when Henry Cavendish investigated the composition of atmosphere. He subjected a mixture of dioxygen and air to electric spark. The oxides of nitrogen thus formed were separated by dissolving them in an alkaline solution. Even after repeated sparking, a small residual gas (1/120th part of the original volume of air) was always left behind which was neither dinitrogen nor dioxygen. What Cavendish had actually isolated was, of course, a mixture of the noble gases, but he could not characterize this as component of the air. It would be interesting for you to know that his figures are remarkably close to the volume contents of the noble gases in the atmosphere as we now know them. The importance of this observation was not realized until 1894. In 1894, a new turn came in noble gas chemistry with the Lord Rayleigh's observations. He made precise and accurate measurements of the densities of common gases and found to his surprise that although one litre of atmospheric dinitrogen (obtained from air by the removal of O_2 , CO_2 and H_2O) weighed 1.2574 g, one litre of pure dinitrogen (prepared by the decomposition of ammonia) weighed only 1.2506 g under the same conditions. Reyleigh tried to correlate this discrepancy with the Cavendish's residual gas and suspected the presence of a previously

unidentified element in the atmosphere. In that very year, both Sir William Ramsay and Rayleigh treated "atmospheric dinitrogen" with heated magnesium and obtained solid magnesium nitride (Mg_3N_2). The small amount of residual gas left after the reaction was identified on the basis of spectroscopic studies, as a new element which was named argon (Greek word = lazy or idle) because it would not react.

You remember Mendeleev's periodic table which had no place for a new and inert gaseous element. This led Ramsay to suggest that a whole new group of such elements might be present. In 1898 Ramsay and Travers carried out fractional distillation of the residual unreactive gas named argon. As a result, they characterized another element and named it neon (Greek word = new). Further analysis of the less volatile fraction and spectroscopic characterization, led to the discovery of other two elements krypton (Greek word = hidden) and xenon (Greek word = strange).

As you would just appreciate, the history of the discovery of helium merits separate discussion. As early as 1869, French astronomer Janssen came to India. He made certain spectroscopic studies of the rays of the sun at the time of eclipse. He observed a new yellow line, differing in position from the D lines of sodium, in the solar spectrum so obtained. This led British scientist Frankland and Lockyer to conclude that the sun contained a new element which they naturally named helium (Greek word = sun). All efforts to discover this element on the earth were unsuccessful until 1895. In 1895, Ramsay while searching for argon, examined the gases obtained from heating uranium minerals. He obtained a gas from cleveite which had a spectrum identical with that of helium in the sun's spectrum. Five years later he and Travers isolated helium from a sample of atmospheric neon.

The radioactive member of the group radon was first identified in 1902 by Rutherford and Soddy as a decay product of radium. The name finds its origin from radium and the termination 'on' was adopted from the analogy of names for noble gases.

The distinctive discovery of the noble gases was recognized by the Nobel Prize, the highest International Award for a scientist. Sir W. Ramsay received the Nobel Prize in Chemistry for the year 1904 for the discovery of the noble gases in air and their place in the periodic table. The Physics prize of the same year was awarded to Lord Rayleigh for investigations of the densities of the common gases and for the discovery of argon in the course of these studies.

13.11.3 Occurrence and isolation

All the noble gases occur as minor constituents of the atmosphere, though the radioactive and very rare element radon is not present in constant proportion. Their total abundance in dry air is 1% by volume. Table 13.11 gives the abundance of the noble gases in the atmosphere. Helium is also present in natural hydrocarbon gases. It is also found occluded in some uranium minerals like monazite, *etc.* In both sources it is probably formed

by α particles emission during radioactive disintegration of some nuclides present. Helium is the second most abundant element in the universe (23% compared to 76% dihydrogen) although its terrestrial abundance is very low.

Helium, neon, argon, krypton and xenon are obtained commercially from liquid air by fractional distillation. Radon is a product of radioactive disintegration of a element (for example radium and actinium). It may also be obtained by isolating it from the gas produced in an acidified solution of radium chloride.

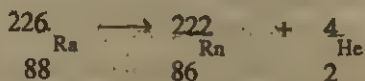


TABLE 13.11: Some properties of the noble gases

Property	He	Ne	Ar	Kr	Xe	Rn
Atomic number	2	10	18	36	54	86
Outer shell electronic configuration	1s ²	2s ²	3s ²	4s ²	5s ²	6s ²
		2p ⁶	3p ⁶	4p ⁶	5p ⁶	6p ⁶
First ionization energy (kJ mol ⁻¹)	2372	2080	1520	1351	1170	1037
van der waals radius (pm)	140	154	188	202	216	—
Melting point (K)	(a)	27	87	119.8	164	211
Boiling point (K)	4.0	24.4	83.6	115.8	161	202
Heat of vapourization, ΔH_{vap} (kJ mol ⁻¹)	0.09	1.84	6.27	9.66	13.68	18.00
Abundance in dry air (ppm) by volume	5.24	18.18	93.40	1.14	0.087	Variable traces

(a) : Helium is the only liquid which cannot be frozen by reducing temperature alone. Pressure must also be applied.

13.11.4 General Trends

The properties and the general trends in properties of the noble gases are summarized in Table 13.11.

All the noble gases are colourless, odourless and tasteless. They are monoatomic in the gaseous state as suggested by the relatively high ionization potentials. They remain gaseous at temperatures at which most of the other elements are liquids and solids.

Their boiling points, melting points and heats of vapourization are extremely low. These properties indicate the absence of strong chemical bonds. Since all the valence electrons are paired in the ground state of the atom, only weak interatomic forces (van der Waals type) operate to hold the atoms together in the liquid and solid states. The increase in values with atomic mass points towards the increasing polarizability of the larger and loose electron clouds of the elements. Weak interatomic valency forces

result in large atomic radii. Such radii are called non-bonded van der Waals radii and increase on descending the group as expected.

Their ionization energies are of very high order. With increasing atomic size there is a decrease in ionization energy. It is relatively difficult to liquefy these gases as their atoms are held only by weak forces. The process of liquefaction becomes easier with increase in size as the van der Waals forces become stronger in nature.

Helium is unique in some of its properties. When helium is cooled under one atmosphere pressure, it liquefies at 4.12K. It acquires the normal properties of a liquid (helium—I) until it is cooled to 2.18K. This liquid at 2.18K, with some abnormal characteristics, is called helium-II. It has been referred to as the 'fourth state of matter'. The liquid is a superfluid, *i.e.*, its viscosity is almost zero and it can creep out of the vessel in which it is contained in defiance of gravity. It is unusually a better conductor of heat and electricity than copper metal.

13.11.5 Compounds of the noble gases

No real compounds of the noble gases were known until 1962. Since then rapid progress has been made in the field of noble gas compounds. Bartlett, in the course of his investigation of various reactions of fluorine with platinum and its salts in a glass apparatus, observed the formation of a red solid, $O_2^+ [Pt F_6]^-$. The formation of this compound involves the loss of an electron from molecular oxygen.

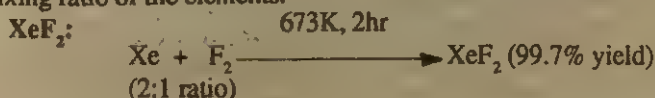


By the consideration that the first ionization energy of $O_2 (O_2 \rightarrow O_2^+ + e^-)$ is close to the first ionization energy of xenon ($Xe \rightarrow Xe^+ + e^-$), Bartlett reasoned that xenon might form a compound with $Pt F_6$ similar to the dioxygenyl hexafluoroplatinate (V), $O_2^+ [Pt F_6]^-$. In June 1962, he could actually prepare a yellow-red powder corresponding to $Xe^+ [Pt F_6]^-$ by interaction of $Pt F_6$ with Xe.



This was the beginning of the research in an extremely challenging field of noble gas compounds. Since then many compounds have been isolated and characterized, *e.g.*, chemical compounds between fluorine and also oxygen and the noble gases krypton, xenon and radon. However, the chemical behaviour of xenon has drawn most of the attention and only the compounds of xenon will be described briefly here.

Xenon forms a number of compounds with fluorine. The best characterized fluorides of Xe are XeF_2 , XeF_4 and XeF_6 . Each of them is prepared by direct interaction of Xe and F_2 in a sealed nickel or monel container. The product obtained depends on the temperature, pressure and mixing ratio of the elements.

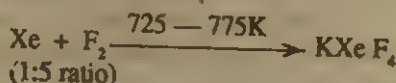


The heated mixture is subsequently cooled. A white solid of XeF_2 separates on vacuum sublimation. Both XeF_4 (0.3%) and XeF_6 (negligible) are also formed.

XeF_2 can also be prepared by exposing the gas mixture to sunlight at one atmosphere pressure for a few hours. On exposing a mixture of Xe and OF_2 to sunlight, XeF_2 separates.

XeF_4 : Pure XeF_4 is difficult to prepare by the usual thermal methods. It usually separates together with XeF_2 and XeF_6 . It is difficult to remove XeF_2 by fractional distillation (similar vapour pressure at room temperature). XeF_6 can be easily separated (discussed later).

Since XeF_6 is easily removed, so it is good to employ an excess of F_2 to reduce the formation of XeF_2 .



XeF_6 : Synthesis of XeF_6 requires vigorous conditions.

573 - 673K, 10 - 20 hr, 50 - 200 atm

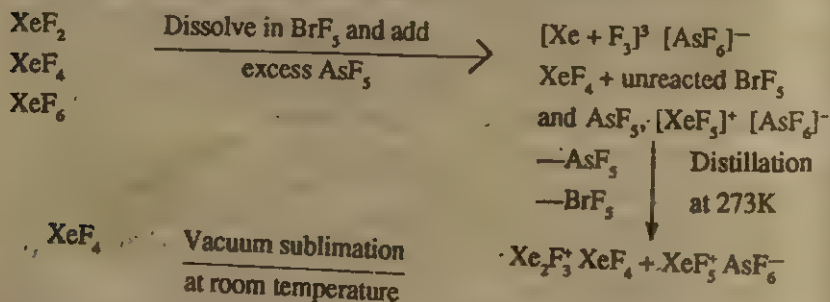


A 95% yield is obtained together with impurities of the kind XeF_2 , XeF_4 and XeF_4 .

The xenon fluorides, XeF_2 , XeF_4 and XeF_6 are white crystalline solids at room temperature, melting at 402K, 362-373K and 322.6K respectively. XeF_6 is the most volatile (vapour pressure 25mm at 298K). They are exothermic compounds. XeF_4 and XeF_6 get hydrolysed.

Purification of XeF_4

It is always contaminated with some amounts of XeF_2 and XeF_6 . It can be purified by making use of its inability to donate fluoride ion to AsF_5 acceptor. Impure XeF_4 is dissolved in BrF_3 and treated with an excess of AsF_5 . XeF_2 and XeF_6 form non-volatile salts $[\text{Xe}_2\text{F}_3]^+ [\text{AsF}_6]^-$. Unreacted BrF_3 and AsF_5 are distilled off at 273K. Pure XeF_4 is then obtained by vacuum distillation at room temperature.



XeF_4 Vacuum sublimation
at room temperature

XeF_6 can be further purified by taking advantage of its ability to form stable compounds with NaF. The impurities do not form stable complexes with NaF and can be pumped off at 325K. The stable complex, 2NaF. XeF_6

is then heated to 400K under vacuum when it gives pure XeF_6 .

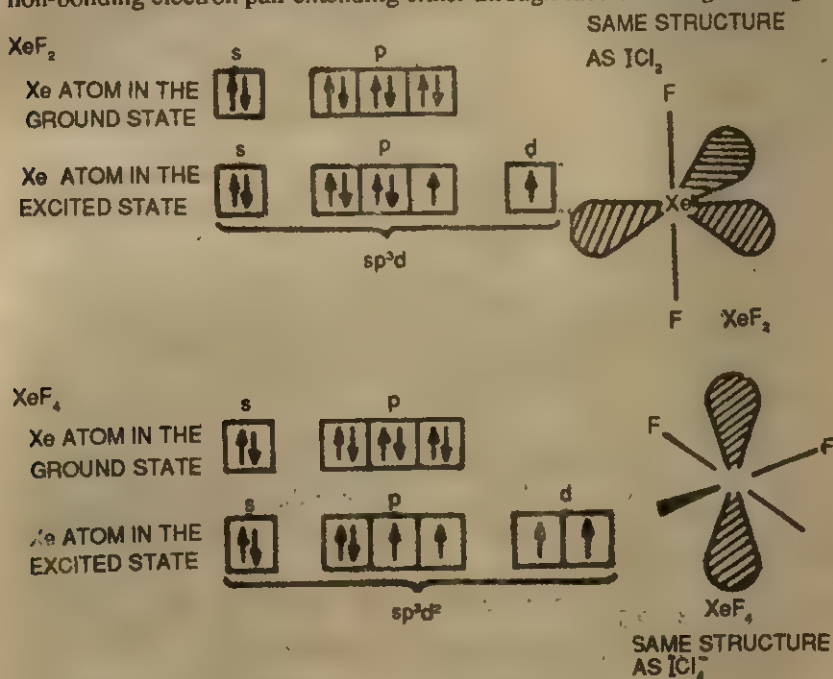
KrF_2 has been characterized but no stable compounds of He, Ne or Ar are known.

Structure of xenon fluorides

In the formation of XeF_2 , one of the 5p electrons in Xe is uncoupled and promoted to the 5d orbital. The two unpaired electrons form bonds with two fluorine atoms. Thus, Xe assumes sp^3d hybridization. Because of the presence of 3 lone pairs of electrons, the Xe and F atoms lie in a straight line (linear disposition).

In XeF_4 , two of the 5p electrons are promoted to the 5d orbitals. In the process, Xe assumes sp^3d^2 hybridization. Because of the presence of two lone pairs of electrons, the molecule acquires a square planar structure.

In XeF_6 , three 5p electrons are promoted to the 5d orbitals. In the process, Xe assumes sp^3d^3 hybridization. Because of the presence of one lone pair of electrons, the molecule acquires a distorted octahedron with a non-bonding electron pair extending either through face or through an edge.



13.11.5 Uses of Noble Gases

The noble gases have many uses, some of which they derive from their inactive properties.

Helium: Its most versatile uses are based on its inertness, low molecular mass and ability to remain as a liquid at temperatures approaching the absolute zero and contain unusual properties possessed by liquid helium and no other liquid. It is used in filling air ships and weather balloons due to its

non-inflammability and low density. Thus, it eliminated the fire hazard possible when dihydrogen was present.

Helium with dioxygen is used by deep sea divers, in place of dinitrogen-dioxygen mixtures. It is less soluble than dinitrogen in the blood stream. The use of helium prevents the danger of a pathological condition called 'bends' when the divers come to the surface and the pressure releases. It is caused by the formation of bubbles of dinitrogen in blood veins which block circulation and can be fatal. In hospitals, mixtures of helium and dioxygen are used to treat respiratory diseases, such as, asthma. The lightness and rapid diffusion reduce the muscular effort involved in breathing.

Metals become superconducting at liquid helium temperatures. The underground transmission of electric power through metal cables suspended in liquid helium is being explored currently. The large electromagnets required in a nuclear fusion reactor also utilize huge quantities of liquid helium to render metals superconducting.

Helium is used to provide an inert atmosphere for melting and welding of easily oxidizable metals and for many metallurgical operations and chemical processes. It is also used as carrier gas in chromatography. It is used as a cooling agent when extremely low temperatures are required. Luminescent tubes are also filled with helium.

Neon: It is used in the neon lamps and signs. A brilliant orange-red glow is produced when electric current is passed through an evacuated glass tube containing neon gas at low pressure.

Argon: It is used in electric light bulbs to replace air which would destroy the hot filament by oxidation. Argon with mercury vapours is used in fluorescent tubes. Geiger-counter tubes are also filled with argon.

Krypton and Xenon: A krypton-xenon photographic flash tube has been developed. High speed photographic exposures can be taken using this tube. Xenon is also used in radio and television tubes.

Radon: It is used in radio-therapy in treatment of cancer. Except helium and radon, all gases are used in lasers and in filling luminescent electric tubes for various advertising and other purposes. They emit beautifully coloured penetrating light.

SELF ASSESSMENT QUESTIONS

Multiple Choice questions

13.1 Put a tick (✓) mark against the most appropriate choice:

- (i) A gas that cannot be collected over water is
(a) N_2 (b) O_2 (c) SO_2 (d) PH_3 (IIT 1985)
- (ii) Which one among the following pairs of ions cannot be separated by H_2S in dilute hydrochloric acid?
(a) Bi^{3+} , Sn^{4+} (b) Al^{3+} , Hg^{2+} (c) Zn^{2+} , Cu^{2+} (IIT 1986)
- (iii) The compound which gives off dioxygen on moderate heating is:
(a) Cupric oxide (b) Mercuric oxide
(c) Zinc oxide (d) Aluminium oxide (IIT 1988)
- (iv) The oxide that gives hydrogen peroxide on treatment with a dilute acid is :
(a) PbO_2 (b) Na_2O_2 (c) MnO_2 (d) TiO_2 (IIT 1985)

- (v) Bromine can be liberated from KBr solution by the action of :
 (a) Iodine solution (b) Chlorine water.
 (c) Sodium chloride (d) Potassium iodide
- (vi) Which of the followings oxidizing agents is used in the preparation of chlorine from concentrated hydrochloric acid ?
 (a) MnO_2 (b) KMnO_4 (c) H_2SO_4 (d) KNO_3
- (vii) Which of the followings acts as reducing agent ?
 (a) HCl (b) H_2SO_4 (c) HNO_3 (d) Cl_2
- (viii) Which of the following elements does not show allotropy?
 (a) Oxygen (b) Nitrogen (c) Sulphur (d) Phosphorus
- (ix) Which of the following electron configurations does not represent non-metals?
 (a) 2,8,7 (b) 2,8,5 (c) 2,8,2 (d) 2,8,6
- (x) Which of the following statements is not correct?
 (a) Halogens are found in the combined state in the earth's crust.
 (b) Sulphuric acid is a viscous liquid
 (c) Hydrogen sulphide gas is employed in qualitative analysis of anions and cations.
 (d) Ammonia is manufactured by Ostwald's process.
- (xi) Which of the following hydrogen halides has the maximum boiling point?
 (a) HF (b) HCl (c) HBr (d) HI
- (xii) Which of the following halogens is the most oxidant?
 (a) F_2 (b) Cl_2 (c) I_2 (d) Br_2
- (xiii) Which of the following elements does not involved orbitals ?
 (a) O (b) Xe (c) S (d) Cl
- (xiv) Which of the following oxides does not cause acid rain ?
 (a) SO_2 (b) NO_2 (c) CO_2 (d) P_4O_{10}
- (xv) Which of the following halogens is the most electronegative?
 (a) F_2 (b) Cl_2 (c) Br_2 (d) I_2
- (xvi) Which of the following species is the polyhalide ion ?
 (a) ClF_3 (b) BrF_4 (c) ICl_2^- (d) IF_7

13.2. Fill in the blanks:

- (i) Thermal decomposition of _____ gives dioxygen gas.
 (ii) The reaction of water on _____ gives dioxygen gas.
 (iii) Ozone is formed in the _____ by a photochemical reaction.
 (iv) In the normal _____ ice, each oxygen atom is _____ surrounded by _____ other oxygen atoms.
 (v) Hydrogen peroxide is manufactured by the _____ of organic compound.
 (vi) _____ is used for the continuous supply of H_2S gas in the laboratory.
 (vii) Sulphur trioxide gas from the catalytic chamber is passed through sulphuric acid to obtain _____.
 (viii) The molecular formula of hypo is _____.
 (ix) Thiosulphate ion is _____ by iodine to _____.
 (x) Fluorine in all its compounds has an oxidation state of _____.

13.3 Match each item of the right hand column with an appropriate item in left hand column for each of the followings:

- | | |
|---------------------------|----------------------------------------|
| (i) Chlorine | 1. Oxygen |
| (ii) Sodium thiosulphate | 2. Deacon process |
| (iii) Priestley | 3. Ozone |
| (iv) Ramsay | 4. Antichlor |
| (v) Hydrogen | 5. Catalyst |
| (vi) Disinfectant | 6. Copper sulphate |
| (vii) Calcium carbonate | 7. Used in photography |
| (viii) Vanadium pentoxide | 8. Inert gases |
| (ix) Hydrate | 9. Effective in preventing tooth decay |
| (x) Sodium fluoride | 10. An oxidizing agent |
| (xi) Iodine | 11. Most basic |

(xii) Silver bromide

12. Hard water

13.4 Write true (T) or false (F) against each of the following statements:

- (i) Hydrogen sulphide acts as a reducing agent.
- (ii) The dilute sulphuric acid on reacting with copper turnings gives sulphur dioxide.
- (iii) The bleaching properties of both sulphur dioxide and chlorine depend on their reducing nature.
- (iv) For the preparation of dilute sulphuric acid, concentrated sulphuric acid is added to water with constant stirring.
- (v) Chlorine is the most active among halogens.
- (vi) HF is the strongest acid among all the hydrohalic acids.
- (vii) Van der Waals radii of noble gases are smaller than atomic radii.
- (viii) Radon is one of the constituents of the atmosphere.
- (ix) The density of water is maximum at 277k.
- (x) Ozone is not an allotropic form of dioxygen.

SHORT ANSWER QUESTIONS

13.5 (i) In solution chlorine is a stronger oxidizing agent than fluorine. Comment.

(IIT 1984)

(ii) Anhydrous HCl is a bad conductor of electricity but aqueous HCl is a good conductor. Comment.

(IIT 1985)

(iii) Fluorine cannot be prepared from fluoride by chemical oxidation. Comment.

(IIT 1985)

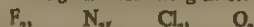
(iv) Arrange the following in order of their increasing acidic character:

(IIT 1985)



(v) Arrange the following in order of their increasing bond length:

(IIT 1985)



(vi) What happens when hydrogen sulphide is bubbled through an aqueous solution of SO_2 ?

(IIT 1985)

(vii) Hydrogen peroxide is a better oxidizing agent than water?

(IIT 1986)

(viii) Arrange the following in the order of their

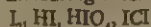
(IIT 1986)

(a) increasing bond strength,



(b) increasing oxidation number of iodine,

(IIT 1986)



(ix) Mention the products formed in the following:

(a) Chlorine gas is bubbled through a solution of ferrous bromide.

(b) Sulphur dioxide gas, water vapour and air are passed over heated sodium chloride.

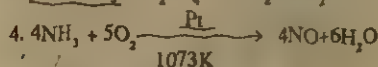
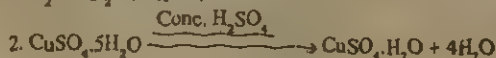
(c) Sulphur is treated with an alkali. (IIT 1986)

(x) The valency of oxygen is generally two whereas sulphur shows valencies of two, four and six.

(xi) Write the balanced equation for: iodate ion reacts with bisulphite ion to liberate iodine. (IIT 1988)

(xii) What is the importance of heavy water with regard to nuclear power stations?

13.6. (a) Comment on the role of the substances underlined in the following reactions:



(b) Name the gases produced in the following reactions:

(i) Potassium chlorate is heated in the presence of manganese dioxide.

- (ii) Zinc is treated with dilute sulphuric acid.
 - (iii) Magnesium is treated with dilute nitric acid.
 - (iv) Dilute sulphuric acid is added to iron pyrites.
 - (v) Copper turnings are heated with conc. sulphuric acid.
 - (vi) A mixture of sodium nitrite and ammonium chloride is heated.
 - (vii) A mixture of common salt and concentrated sulphuric acid is heated.
 - (viii) A mixture of slaked lime and ammonium chloride is heated.
 - (ix) A mixture of manganese dioxide and conc. hydrochloric acid is heated.
 - (x) Copper is treated with concentrated nitric acid.
- (c) What happens when Cl_2 reacts with: (i) alkali metal, (ii) sulphur dioxide solution in water (iii) a non-metal, (iv) sodium hydroxide, and (v) slaked lime ?

Give equations.

- (d) Distinguish between hydrogen chloride and hydrochloric acid.
 (e) Why is chlorine a potential disinfectant ?

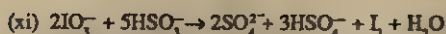
TERMINAL QUESTIONS

- 13.1 (a) Define the term combustion. Is combustion restricted to reactions involving dioxygen ? Explain.
 (b) Why is ozone a more active oxidizing agent than dioxygen ?
- 13.2 (a) Account for the polar character of water and its high boiling point.
 (b) Describe the hydrogen bond.
 (c) Under what conditions does water exist a single H_2O molecule?
- 13.3 (a) Discuss the structure of ice.
 (b) Which metal oxides react with water to form bases?
 (c) What is heavy water and how is it prepared?
- 13.4 (a) How is hydrogen peroxide prepared commercially and in the laboratory?
 (b) Why is H_2O_2 purified by distillation under reduced pressure? What are stabilizers?
- 13.5 (a) Under what conditions does H_2O_2 act as a reductant and oxidant?
 (b) What is the advantage of using H_2O_2 as an oxidizing agent over other such agents?
 (c) Distinguish between oxides and peroxides in terms of electronic structure.
 (d) Write an equation showing that H_2O_2 is an acid.
- 13.6 (a) Starting from elemental sulphur, how would you prepare
 (i) H_2SO_4 , (ii) $\text{Na}_2\text{S}_2\text{O}_3$, (iii) $\text{H}_2\text{S}_2\text{O}_7$
 (b) Describe the contact process for the manufacture of sulphuric acid.
- 13.7 (a) How do you account for the high viscosity and high boiling point of conc. H_2SO_4 ?
 (b) What types of hybridizations of sulphur atom exist in the following ions and molecules?
 SO_4^{2-} , SO_2 , SO_3 , SO_3^{2-} .
- Also mention the oxidation state of sulphur in each.
- 13.8 (a) Comment on the structural features:
 (a) Both SO_2 and SO_3 molecules assume sp^2 hybridization, SO_2 is angular while SO_3 is trigonal in shapes.
 (b) Ozone has resonating structures.
 (c) SO_4^{2-} ion is tetrahedral.
 (d) Sulphur is S_8 while oxygen is O_2 .
 (e) The O-O bond energy in O_2 is much larger than the S-S bond energy in S_8 .
- 13.9 Arrange the halogens in order of decreasing: (a) ionization potential, (b) oxidizing power, (c) bond energy, (d) atomic radius, (e) electronegativity, (f) boiling point, and (g) intensity of colour.
- 13.10(a) Mention the ways in which halogens can acquire noble gas configurations during compound formation.
 (b) Give the various reactions of water and hydrogen with halogens.
 (c) Why is it essential to prepare fluorine by an electrolytic method?

- 13.11. (a) Give a brief resume of the ways in which the behaviour of fluorine differs from the other halogens.
 (b) Name the factors responsible for the differences.
- 13.12 (a) Give reasons for the delayed isolation of fluorine.
 (b) In what way Whytlaw Gray's method for the preparation of fluorine is superior to Moissan's method?
- 13.13. (a) Generally halohalic acids are prepared by the action of conc. sulphuric acid on the appropriate halides. But this method is not suitable for the preparation of HBr and HI, Explain.
 (b) Why does HF tend to associate into bigger molecules? Name two other compounds which also show association. Does association affect the properties of molecule? Explain the effects observed with HF in comparison to other compounds - HCl, HBr and HI.
 (c) Name two sources and four important uses for each of the halogens.
- 13.14. (a) In what ways do the boiling and melting points of the noble gases behave with increasing size of the gas? Explain.
 (b) Give reasons for the low boiling points of the noble gases.
 (c) Light noble gases, He and Ne are not capable of forming many compounds. Explain?
 (d) Discuss the discovery of the noble gases. Why did they remain undiscovered for such a long time?
- 13.15 List some uses of helium and radon.
- 13.16. What are interhalogen compounds. List a few interhalogen compounds of type XX_n ($n = 3, 5, 7$) and predict their molecular shapes from VSEPR theory.
- 13.17. (a) Which of the noble gases are capable of forming compounds? Write formulae to illustrate some of these compounds.
 (b) What are the molecular shapes of XeF_2 and XeF_4 .
 (c) Why were the first successful attempts at preparing compounds of xenon made with fluorine?

ANSWERS TO SELF ASSESSMENT QUESTIONS

- 13.1 (i) (c) (ii) b (iii) b (iv) b (v) b (vi) a (vii) a (viii) b (ix) c (x) d
 (xi) a (xii) a (xiii) a (xiv) d (xv) a (xvi) c
- 13.2 (i) Oxygen rich compound $KMnO_4$ or $KClO_3$ (ii) Na_2O_2 (iii) upper atmosphere (iv) hexagonal; tetrahedrally, four (v) autoxidation, 2 ethylanthraquinone (vi) Kipp's apparatus (vii) oleum (viii) $Na_2S_2O_3 \cdot 5H_2O$ (ix) oxidized tetrathionate ion (x) —1.
- 13.3 (i) 2 (ii) 4 (iii) 1 (iv) 8 (v) 10 (vi) 3 (vii) 12 (viii) 5 (ix) 6 (x) 9
 (xi) 11 (xii) 7
- 13.4 (i) T (ii) F (iii) F (iv) T (v) F (vi) F (vii) F (viii) F (ix) T (x) F
- 13.5 (i) The given statement is wrong, because the hydration energy of F^- is more than that of Cl^- .
 (ii) Anhydrous HCl (covalent) does not furnish any ion, hence, does not conduct electricity. On the other hand aqueous HCl, being an ionic compound furnishes ions and is, thus, a good conductor of electricity.
 (iii) This is because the element fluorine is the most electronegative, and hence, is the most oxidant of all the elements. It cannot be prepared from its fluoride by chemical oxidation.
 (iv) $Na_2O_2 < MgO < ZnO < P_2O_5$
 (v) $N_2 < O_2 < F_2 < Cl_2$
 (vi) Sulphur dioxide is reduced to sulphur and hydrogen sulphide gets oxidized to sulphur.
 (vii) As the oxidation number of oxygen in H_2O_2 is higher ($O_2 = -1$) as compared to that in water ($O = -2$), H_2O_2 is a better oxidizing agent.
 (viii) (a) HI, HBr, HCl, HF
 (b) HI, I_2, ICl, HIO_4
 (ix) (a) $FeCl_3, Br_2$; (b) Na_2SO_4, HCl
 (c) $4S + 6OH^- \rightarrow 2S^{2-} + S_2O_3^{2-} + 3H_2O$
 (x) In the case of sulphur, empty d orbitals are available which can be used for bondings.

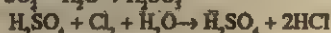
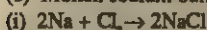


(xii) Heavy water helps in slowing down the speed of neutrons, to be used for fission of uranium. Then it is used as a moderator.

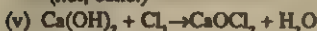
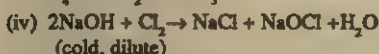
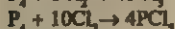
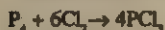
13.6 (a), (1) Reducing agent (2) dehydrating agent (3) oxidizing agent (4) catalyst (5) oxidizing agent.

(b) (i) O_2 , (ii) H_2 , (iii) H_2 , (iv) H_2S , (v) SO_2 , (vi) N_2 , (vii) NH_3 , (viii) HCl , (ix) Cl_2 , (x) NO_2

(c) Molten sodium burns in chlorine with a yellow flame



(iii) White phosphorus burns spontaneously in the atmosphere of Cl_2 producing white fumes of chlorides.



(d) Hydrogen chloride gas in water is called hydrochloric acid. Hydrochloric acid is present as H^+ and Cl^- ions. Here H^+ exists as H_3O^+ .



Due to the presence of H_3O^+ ions, hydrochloric acid exhibits acidic properties.

Hydrogen chloride has a single polar covalent bond. There are no H_3O^+ .

H^+ or Cl^- ions. Thus, it does not exhibit acidic properties.

(e) Chlorine on bubbling through water produces hypochlorous acid which, in turn, decomposes to produce atomic oxygen, the active disinfectant, and hydrochloric acid.

Chemistry of Lighter Metals

(Sodium, Potassium, Magnesium, Calcium and Aluminium)

My advice to those who wish to learn the art of scientific prophecy is not to rely on abstract reason, but to decipher the secret language of Nature from Nature's documents, the facts of experience.

MAX BORN

UNIT PREVIEW

- 14.1 Introduction
- 14.2 Group 1 elements — general characteristics
- 14.3 Sodium and potassium
- 14.4 Some important compounds of sodium and potassium — sodium chloride, sodium carbonate, sodium hydrogen carbonate, sodium hydroxide, potassium chloride and potassium hydroxide
- 14.5 Group 2 elements — general characteristics
- 14.6 Magnesium and calcium
- 14.7 Some important compounds of magnesium and calcium — magnesium chloride, magnesium sulphate, calcium oxide, calcium hydroxide, calcium carbonate, calcium sulphate and plaster of paris.
- 14.8 Hard and soft water — water softening.
- 14.9 Group 13 elements — general characteristics
- 14.10 Aluminium
- 14.11 Some compounds of aluminium — aluminium chloride, aluminium sulphate.
- 14.12 Cement
- 14.13 Biological role of sodium, potassium, magnesium and calcium
 - Self assessment questions
 - Terminal questions
 - Answers to self assessment questions

LEARNING OBJECTIVES

At the completion of this unit, you should be able to :

1. Differentiate between metals and non-metals with reference to their physical and chemical characteristics.
2. Characterize the metals on the basis of their chemical properties, e.g., action of oxygen, water, dilute acids and salt solutions on metals with reference to their physical and chemical properties. Understand the importance of metals in life processes.
3. Describe the trends in relation to the periodic table of atomic and ionic size, density, melting and boiling points, ionization energy, etc. exhibited by the metallic elements.
4. Relate relative ability as reducing and oxidizing agents to position with periodic table and to oxidation state.
5. Comment on the group similarities among the members of each group and exceptions to group similarities exhibited by the first member of each group with regard to the other members of the group.
6. Account for the source of metals in native and combined forms.
7. Account the factors influencing the choice of methods used in reducing a metal ore.
8. Describe the following processes:
 - Calcination, roasting, aluminothermy, leaching, electrolytic reduction, smelting, electrolytic refining, tempering, bessemerization, etc.
9. Learn the chemistry (occurrence, extraction, properties etc.) of the following metals: sodium, potassium, magnesium, calcium and aluminium.
10. Comment on the storage of sodium and calcium.
11. Explain the working principle of the electrolytic cells used in the extraction of sodium, magnesium, calcium and aluminium.

12. Give the composition and uses of the alloys spanning this unit.
13. List some of the main uses of the metals included in this unit.
14. Give the chemical formulae of the various minerals and ores covered in this unit.
15. Describe the preparation and properties of the various compounds included in this unit.

14.1 INTRODUCTION

Elements, based upon their physical and chemical properties and nature of their compounds, have been classified into three groups : metals, non-metals and metalloids. Non-metals (Unit 12 and 13) have already been introduced to you.

Most of the elements are metals and are contained in all groups (except group 18) of the periodic table. Metallic elements are located below and to the left of the stepwise division in the p-block of the periodic table. Metals have a wide variety of characteristics, but all metals share certain general physical and chemical properties. The general properties that distinguish between metals and non-metals have already been discussed in Unit 12. The position of metals, non-metals and metalloids is shown in Fig. 14.1.

H								He
Li	Be	B	C	N	O	F		Ne
Na	Mg	Al	Si	P	S	Cl		Ar
K	Ca	Ga	Ge	As	Se	Br		Kr
Rb	Sr	In	Sn	Sb	Te	I		Xe
Cs	Ba	Tl	Pb	Bi				Rn

Labels and arrows in the diagram:

- ← NON-METAL (pointing to H)
- METALS (pointing to Li, Na, K, Rb, Cs)
- TRANSITION ELEMENTS (pointing to Be, Mg, Ca, Sr, Ba)
- METALS (pointing to Al, Si, Sn, Pb)
- BRIDGING ELEMENTS BETWEEN ELECTROPOSITIVE AND ELECTRONEGATIVE ELEMENTS (METALLOIDS) (pointing to Ga, Ge, As, Sb, Te)
- NON-METALS (pointing to He, Ne, Ar, Kr, Xe, Rn)

Fig. 14.1 Metals, non-metals and metalloids in the periodic table.

The apparent difference between the properties of metals and non-metals is due to the arrangement of electrons in their atoms. Further the physical properties of metals can be explained on the basis of bonding, combining one metallic atom with another similar metallic atom (metallic bonding).

Several of the metals are rare and have little practical value, but some metals are abundant, e.g. Cu, Al, Ca, Fe, Na, Zn, Mg and Ti. Our civilisation is based upon all such metals. Metals are useful in varied type of industries – automobiles, agricultural machinery and implements,

aeroplanes, buildings, warships, ships, defence equipments *etc.* Metals play a vital role as catalysts in certain chemical processes, *e.g.*, hydrogenation of vegetable oils, manufacture of ammonia, sulphuric acid, nitric acid, hydrochloric acid, *etc.*, and manufacture of synthetic dyes organic solvents, drugs, general medicines, explosives, plastics, *etc.*

Metals and their compounds are useful to mankind. Iron was the first trace element shown to be essential in the human diet. It is a component of haemoglobin. Additional trace metals have been found to be essential to human nutrition: Cu, Mn, Zn, Co, Mo and Cr. Cobalt is a component of vitamin B₁₂. Both manganese and molybdenum are involved in formation of enzymes. Chromium is useful for glucose metabolism. Zinc is present in some of the enzymes and in the hormone insulin. Copper is involved in absorption and mobilisation of iron required for haemoglobin. Metals form an important component of the mineral wealth of a country.

In this unit, we shall study about the chemistry of sodium and potassium (group 1); magnesium and calcium (group 2); and aluminium (group 13). They are called lighter metals because of their low density. Compounds of some of these elements, such as soda ash, common salt, baking soda and lime are useful in our daily life. Monovalent sodium and potassium ions and bivalent magnesium and calcium ions are found in large proportions in biological fluids. They maintain ion balance and nerve conduction. Aluminium is used extensively as a structural metal. Its strength can be improved by alloying with magnesium or copper.

14.2 GROUP 1 ELEMENTS – GENERAL CHARACTERISTICS

The s-block elements consist of six alkali metals of group 1 and the six alkaline earth metals of group 2. The last member of each group, francium (Fr) and radium (Ra) are radioactive.

The metals of group 1 are soft and have low densities and melting and boiling points. With their ns^1 electron configuration, they are the most reactive of the metals. The elements and their compounds are chemically very similar owing to their similar valence shell electron configuration. Differences that exist primarily reflect the variation in atomic radius. Their reactivity within the family, generally increases with increasing atomic number as ionization energy decreases. Because of low ionization energies, the metals are strong reducing agents and can reduce almost any electronegative element like N, P and S. These elements are electropositive metals. As usual, the first member of the group, lithium is much more electronegative than the other members of the group. Further lithium differs in chemical behaviour from the second member, *i.e.*, sodium of the group. This is because of the significant difference in their sizes and electronegativity values. It resembles magnesium of group 2. The ions of both the metals have the same size.

All the metals in the group have body centred cubic structures at room temperature. The relatively low melting and boiling points, densities, etc. are consequences of the fairly weak bonding forces, since each atom can furnish only one electron for metallic bonding. Because their outer electrons are loosely held, the metals are good electrical and thermal conductors. Alkali metals, in their compounds, exhibit the +1 oxidation state. Their compounds are generally ionic. It is easy to excite the valence electrons of these metals to higher energy states. When the excited electrons return to the ground state, there is emission of radiation in the visible region. Now when one of their salts is introduced in the bunsen burner flame, lithium salts impart a beautiful red colour to the flame, sodium salts give brilliant yellow colour, whereas potassium salts produce a violet coloured flame. These colours are intense enough to serve as useful qualitative tests called flame tests for the detection of these metals. On irradiation with light, the elements emit electrons, and thus, potassium and caesium find use in photoelectric cells.

These elements, because of their reactive nature, are always found combined with other elements. Some of the important general properties of the group 1 elements are given in Table 14.1

TABLE 14.1: Properties of group 1 elements

Property	Li	Na	K	Rb	Cs
Atomic number	3	11	19	37	55
Electron structure	(He)2s ¹	(Ne)3s ¹	(Ar)4s ¹	(Kr)5s ¹	(Xe)6s ¹
Abundance in earth's crust (ppm)	65	28300	25900	310	7
Atomic (metallic) radius (pm)	155	190	235	248	247
Ionic radius, M ⁺ (pm)	60	95	133	148	169
Melting point (K)	453	370.8	336.8	312	301.5
Boiling point (K)	1590	1155.9	1039	961	963
Ionization energy (kJmol ⁻¹)	520	495	418	403	374
Electronegativity	1.15	1.0	0.9	0.9	0.85
Electron affinity (kJmol ⁻¹)	-57	-21	—	—	—
Density (g/cm ³)	0.53	0.97	0.86	1.53	1.87
Reduction potential E° (V)	-3.04	-2.71	-2.93	-2.99	-3.02
(M ⁺ + e ⁻ → M)					

14.3 SODIUM AND POTASSIUM

Both sodium and potassium were isolated in 1807 by Humphry Davy by the electrolytic dissociation of their respective hydroxides. The electrolytic reduction itself speaks of the difficulty with which their ions are reduced to the metallic state. They are good reducing agents. The power of these metals as reducing agent is shown by the vigour with which they reduce water to dihydrogen. The reduction potential (Table 14.1) measures their strong tendency as reducing agents.

14.3.1 Occurrence

Alkali metals are widely distributed in nature. They are too reactive to occur uncombined. Both sodium and potassium are abundant in the

earth's crust (Table 14.1). Sodium is the fifth most abundant of all the elements in the earth's crust. Sodium chloride, the richest source of sodium is known to exist since ancient times. Sodium chloride and other compounds of sodium and other alkali metals are soluble in water. They are found in abundance in sea water. Some of the common naturally occurring salts of sodium found as deposits are rock salt (sodium chloride), Chile saltpetre or caliche (sodium nitrate), sodium carbonate and borax.

Potassium chloride occurs in nature in small amounts as compared to sodium. Carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), kainite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and saltpetre (KNO_3) are the well known natural rock deposits of potassium.

Both sodium and potassium are found associated with a large number of complex silicate rocks such as feldspars, of which the very abundant albite $\text{Na}[\text{Al}(\text{SiO}_2)_3]$ and orthoclase, $\text{K}[\text{AlO}_2(\text{SiO}_2)_3]$ are typical. Weathering reactions convert all the deposits of sodium and potassium into soluble salts which are carried to the sea. Because most of the compounds of the alkali metals are soluble in water, their rich deposits are found in evaporated inland seas. Their selective crystallization has produced relatively pure deposits of sodium and potassium chlorides, alongwith smaller amounts of other halides, sulphates, nitrates and carbonates. Both the Dead Sea and Great Salt Lake are highly rich in alkali salts from which K_2SO_4 and Na_2SO_4 and other compounds are obtained.

14.3.2 Isolation of Sodium and Potassium

Alkali metals are strong reducing agents, and hence, cannot be isolated by reduction of their oxides or other salts. Sodium and potassium are, therefore, obtained by electrolytic reduction of their molten chlorides. A concentrated solution of sodium chloride called brine (or KCl) can also be used for electrolysis.

Electrolysis of Molten Sodium Chloride

Sodium is obtained on commercial scale by electrolytic dissociation of molten sodium chloride in a cell. The electrolytic cell's layout (Down's cell) is shown in Fig. 14.2. Molten sodium chloride, 60% mixed with calcium chloride, 40% (acts as flux and lowers the melting point, i.e. the operating temperature could, thus, be reduced from 1075K to 778K) is placed into the cell and electrolysis is carried out. Sodium is deposited at the circular cathode and chlorine gas is discharged at the anode (graphite). Molten sodium is siphoned from the cathode compartment and led into vessels. Electrolytic products (Na and Cl_2) react readily so the cell is provided with a protective diaphragm as to keep them apart. The hood over it channels the escaping chlorine gas.

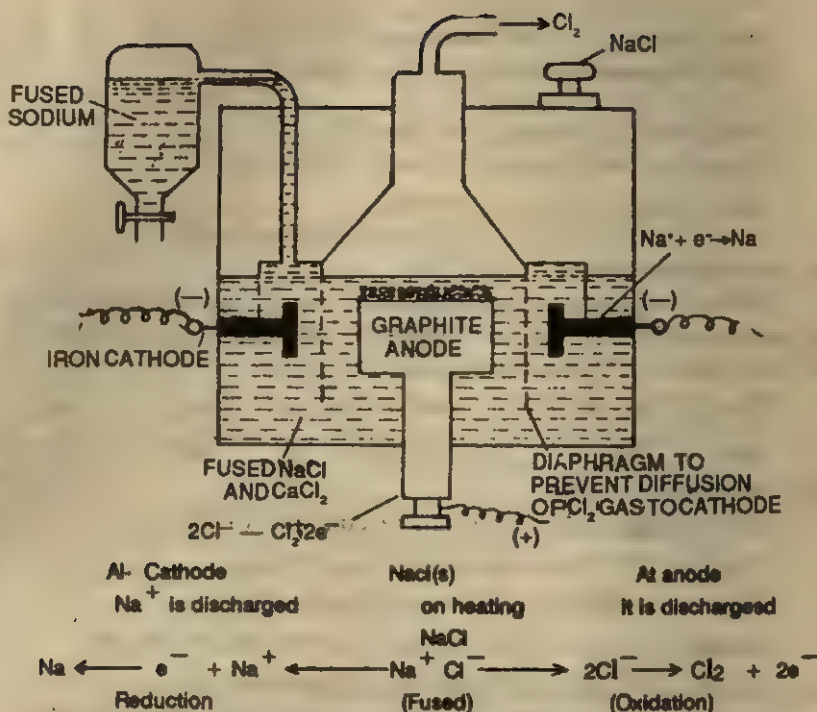


Fig. 14.2 The Down's cell for electrolyzing molten sodium chloride to produce molten sodium and chlorine gas.

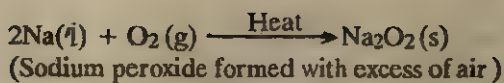
Potassium is produced on a relatively small scale, since this element offers few technical advantages over the less costly sodium. It is produced by the electrolytic reduction of either molten potassium chloride or potassium hydroxide. In USA, it is now being produced by the reaction of sodium with fused potassium chloride. This reaction looks somewhat difficult. For the fused salts, the regular electromotive series does not hold good.

14.3.3 Properties of Sodium and Potassium

Both sodium and potassium are light and soft metals. They can be cut with a knife. They are silvery white and tarnish rapidly in air and become covered with a film of oxide. Because of their highly reactive nature, they are usually stored under kerosene oil to prevent the metals from exposure and moisture. Potassium is more reactive than sodium (reactivity increases down the group). Potassium react so vigorously with water that dihydrogen formed catches fire.

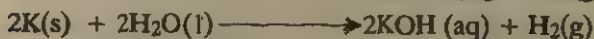
(i) Reaction with oxygen

Sodium and potassium react with dioxygen. They tarnish in air and soon become coated with a film of oxide. They burn readily in air to form oxides and peroxides.



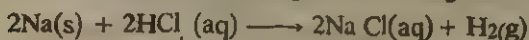
(ii) Reaction with water

Sodium and potassium react with cold water to give dihydrogen and the metal hydroxide. They react vigorously, fizzing and skating about on the water surface. They reduce water to dihydrogen.



(iii) Reaction with acids

Sodium displaces dihydrogen on reacting with dilute acids.



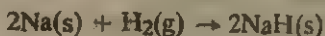
Potassium also reacts with dilute acids producing dihydrogen.

(iv) Reaction with solution of salts (displacement reaction)

Sodium and potassium can displace less active metals from their salt solutions. (Unit 10).

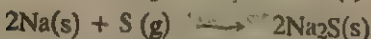
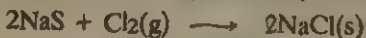
(v) Reaction with dihydrogen

Sodium and potassium on heating, react with dihydrogen forming hydrides.



(vi) Reaction with non-metallic elements

Sodium and potassium on heating react with halogens and sulphur to form halides and sulphides respectively.



14.3.4 Uses of Sodium and Potassium

The various uses of sodium and potassium are listed below:

(i) Molten sodium or its alloy with potassium is used as a coolant in nuclear reactors. (ii) Sodium vapour lamps are used for street lighting. The yellow luminescence of sodium vapour was used during the flight of one of the Soviet space rockets when it was necessary to locate it in the space. (iii) An alloy of sodium and lead is used in the manufacture of tetraethyl lead (TEL), an essential 'antiknock' additive for petrol.

Pb + 4Na + 4C₂H₅Cl → (C₂H₅)₄Pb + 4NaCl (iv) Sodium, because of its reducing nature, is used in the manufacture of drugs and dyes and in

the metallurgy of metals such as titanium and zirconium. It is also used as a reagent in organic analysis. (v) Sodium wire is used in electrical circuits for special applications. (vi) Amalgam of sodium and potassium (Metal + mercury) is used as reducing agent. (vii) Sodium and potassium are used in the preparation of the various compounds given below :

1. **Caustic Soda, NaOH:** Used in the production of rayon, cleansers, textiles, soap, paper, *etc.*, used to purify petroleum products from acids. It is an important material for chemical industry. 2. **Soda ash, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$:** Used in the manufacture of glass, in house for laundry and other purposes. It is an important chemical for industry and is also a substitute for NaOH when a weaker base is required. 3. **Baking soda, NaHCO_3 :** Used for baking and other household purposes. 4. **Sodium chloride, NaCl:** Used as table salt and in canning of foods (to prevent putrefaction). Its solution is used in hospitals. It is a good source of all other compounds of sodium and chlorine. 5. **Sodium nitrate, NaNO_3 :** Used as nitrogenous fertilizer. 6. **Sodium cyanide, NaCN :** Used in the extraction of gold and silver. 7. **Potassium chloride** is used as a fertilizer and **Potassium nitrate** is an essential constituent of gun powder.

14.4 SOME IMPORTANT COMPOUNDS OF SODIUM AND POTASSIUM

Group 1 metals always form compounds in which the metals have the oxidation number +1. The compounds are all ionic and they are all soluble in water. Some industrially important compounds of sodium and potassium are : halides, carbonates, sulphates, and hydroxides.

14.4.1 Sodium Chloride

Sodium chloride is one of our most abundant minerals. Sea water contains about 3.5% of soluble salts, the most common of which is sodium chloride (2.7 to 2.9%). Most of the common salt, particularly in tropical countries, comes from sea water. Production methods of salt vary with the locality and with the use to be made of the salt. India has a long coastal line. It produces about 50 lakh tons of salt annually by solar evaporation. Gujarat produces a major share of the salt produced in our country. The hot, dry and windy climate help in the fast evaporation of water from the salt fields containing sea water. Natural salt contains other soluble salts—sodium sulphate, calcium sulphate, calcium chloride, and magnesium chloride as impurities which make it unsuitable for many of its uses. Sodium chloride, mixed with chlorides of magnesium and calcium, absorbs atmospheric water causing the salt to cake. Salt is purified by dissolving it in water and then by filtering to remove insoluble impurities. The solution is then saturated with hydrogen chloride gas. Crystals of pure salt separate out leaving behind in the solution more soluble

chlorides of calcium and magnesium. Some of the impurities such as calcium sulphate which are less soluble than the salt crystallize out with the salt and are later removed. Advantage can also be taken of the decreasing solubility of calcium sulphate in sodium chloride solution as the temperature is raised above 353K. Thus, if the solution or sodium chloride is filtered hot, the resulting solution will not contain much of calcium sulphate.

In countries, with vast deposits of rock salts, the salt is removed by mining or by forcing water down into deposits to form saturated brines, which are then pumped to the surface. Brine, is thereafter, purified.

Sodium chloride is the usual source of all other sodium and chlorine compounds. It is employed in the manufacture of chlorine, hydrochloric acid, sodium hydroxide and sodium carbonate (Fig 14.3). It is an essential component of food. It is present in the blood and hence is necessary for the life process of the human body.

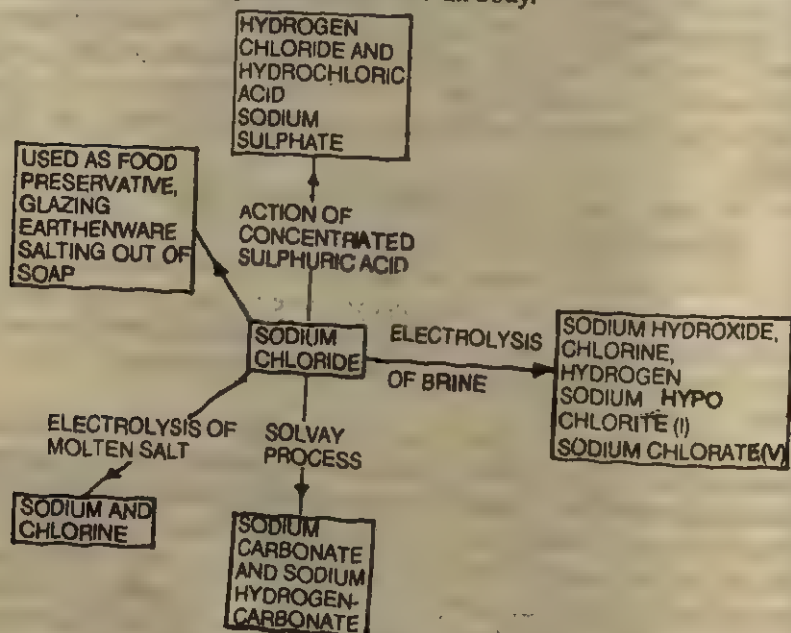


Fig. 14.3 Uses of common salt

Sodium chloride melts at 1081K. Its solubility at 273K is 36g in 100g of water. The solubility does not increase appreciably with rise in temperature.

14.4.2 Sodium Carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$

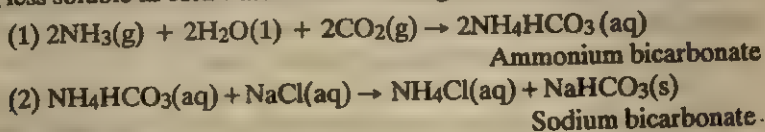
Sodium carbonate is commercially known as soda or washing soda. It is available in three commercial forms :

- (i) Washing soda crystals, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$

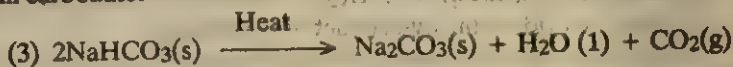
- (ii) Crystals of carbonate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$
- (iii) Soda ash, Na_2CO_3 .

Preparation

Sodium carbonate is manufactured by the ammonia-soda or Solvay process. This process is based upon the reaction of ammonium hydrogen carbonate with a saturated solution of sodium chloride. To get ammonium hydrogen carbonate carbon dioxide is passed through a concentrated solution of sodium chloride (brine) saturated with ammonia. The ammonium hydrogen carbonate solution and sodium ions from the solution interact forming sodium bicarbonate which precipitates being less soluble in cold water. The following reactions take place :



Sodium bicarbonate, a crystalline solid is then heated to produce sodium carbonate.



Carbon dioxide and ammonium chloride obtained in the process are reused.

The Solvay process (Fig. 14.4) involves the following stages :

1. The preparation of ammoniacal brine. A saturated solution of common salt (brine) is passed down a tower fitted with baffle plates.

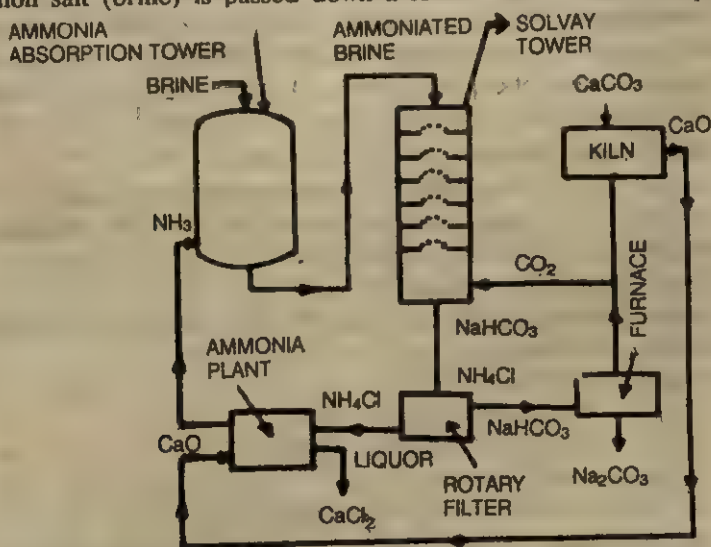


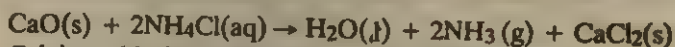
Fig. 14.4. The ammonia-soda (Solvay) process for the manufacture of sodium carbonate.

Ammonia is pumped up from the bottom of the tower. Ammonia mixes with brine and saturates it.

2. **The preparation of sodium bicarbonate.** Carbon dioxide obtained by heating limestone ($\text{CaCO}_3 \rightarrow \text{CO}_2 + \text{CaO}$) is blown through the ammoniated brine passing down the Solvay tower fitted also with baffle plates. These plates ensure the complete mixing of carbon dioxide and ammoniated brine. Here, the fundamental reactions (1) and (2) of the whole process take place to produce sodium bicarbonate.

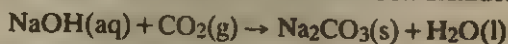
3. **Formation of sodium carbonate.** The sodium bicarbonate (less soluble in cold water), formed as a slurry is fed into the rotary vacuum filter, and the solid mass is then heated in furnaces to produce sodium carbonate (reaction 3). Carbon dioxide formed by the decomposition of sodium bicarbonate is sent back to the Solvay tower.

Calcium oxide obtained on heating limestone (a source of carbon dioxide) is used in the ammonia plant to reproduce the ammonia from the ammonium chloride solution.



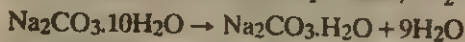
Calcium chloride is the by-product of the process.

In laboratory, sodium carbonate can be prepared by passing carbon dioxide through hot concentrated solution of sodium hydroxide. Sodium hydroxide solution is saturated with carbon dioxide.



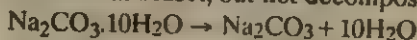
On cooling, crystals of sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) separate out.

Properties : Sodium carbonate is a white crystalline substance containing water of crystallization (10 water molecules). It is efflorescent, i.e., it gives up water of crystallization to the atmosphere on standing and crumbles to powder with the composition, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$.

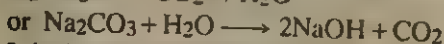
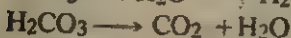
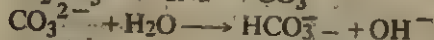
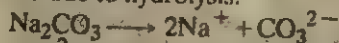


Above 373 K the monohydrate becomes anhydrous powder.

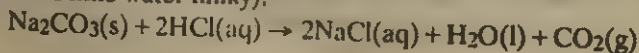
When heated strongly, it first loses all its water of crystallization and then melts at 1125K, but not decompose.



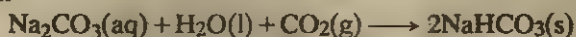
It is soluble in water with evolution of heat. The solution is alkaline in nature due to hydrolysis.



It is decomposed by acids with effervescence giving carbon dioxide (CO_2 turns lime water milky).



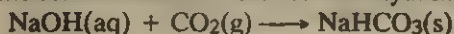
When carbon dioxide gas is passed through a moderately strong solution of sodium carbonate, a white precipitate of sodium bicarbonate forms.



Uses. Sodium carbonate is used (1) in the soap, glass, textile, paper, ceramics and food industries, (2) for softening of water, hence the name washing soda, (3) in the manufacture of sodium hydroxide, borax, water-glass and other sodium compounds, and (4) in the laboratory as a reagent.

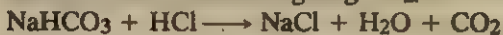
14.4.3 Sodium Hydrogen Carbonate (Baking Soda), NaHCO_3

Sodium hydrogen carbonate is commonly known as bicarbonate of soda or baking soda. The salt is manufactured by the Solvay process. In the laboratory, it is prepared by passing carbon dioxide through a cold concentrated solution of either sodium hydroxide or sodium carbonate.

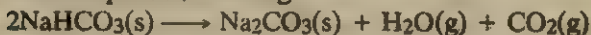


The hydrogen carbonate gets precipitated as white crystalline ppt. Salt, required for household purposes, can be prepared by this method.

The salt reacts with acids giving CO_2 .



It decomposes on heating.



The use of the salt as 'baking powder' depends on this reaction. Mixed with dough (cake, pasteries etc.), the hydrogen carbonate decomposes on heating to give bubbles of CO_2 which make the dough swell, and thus, making it light and fluffy. Commercial variety of the baking powders contain an acidic substance, such as potassium hydrogen tartrate, calcium dihydrogenphosphate. In the presence of moisture, these powders give off CO_2 .

Sodium hydrogen carbonate is a mild antiseptic for skin infections.

14.4.4 Sodium Hydroxide (Caustic Soda), NaOH

Sodium hydroxide is commercially called caustic soda and its solution is sometimes referred to as lye or soda lye.

Sodium hydroxide is usually manufactured by the electrolysis of a concentrated solution of brine, obtained by extraction of underground deposits of sodium chloride by pumping hot water. Various cells are in use for the electrolysis, but all depend upon the following overall cathode reaction.



The result of discharging $\text{H}^+(\text{aq})$ ions is that Na^+ and OH^- ions are left behind in the cathode region.

(i) The Castner-Kellner cell (Fig. 14.5) is a popular cell employed for the manufacture of NaOH . It contains two parts—the mercury cell

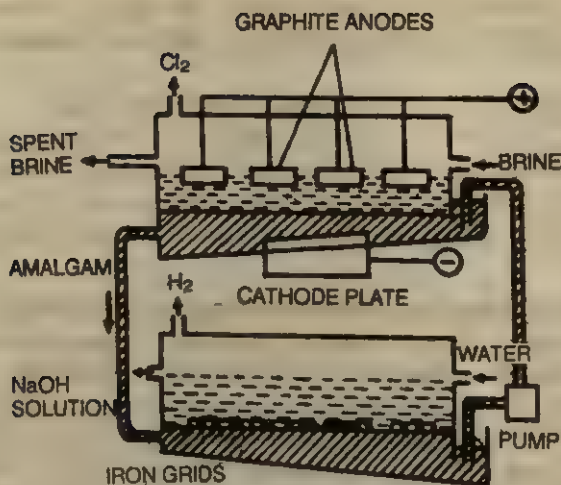
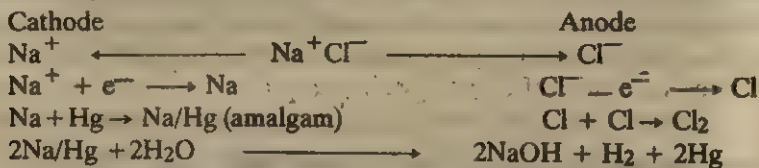


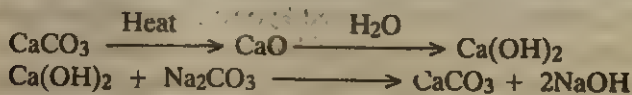
Fig. 14.5 The Castner-Kellner cell

and the soda cell. In the upper mercury cell, on electrolysis, chlorine is discharged at the graphite anodes and sodium at the flowing mercury cathode (liquid cathode) where it reacts with mercury and forms a sodium amalgam.

In the lower soda cell, the amalgam is treated with water. Iron grids float on the surface of the amalgam and the amalgamated sodium reacts with water, liberating hydrogen at the surface of the iron grids giving a solution of sodium hydroxide which is concentrated by evaporation. The liberated mercury is recycled to the upper cell. The reactions taking place are:



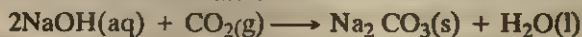
In Gossages' method, milk of lime Ca(OH)_2 obtained from calcium carbonate is treated with a solution of sodium carbonate in large tanks provided with mechanical stirrers. The solution is steam heated.



Insoluble CaCO_3 is filtered out and the NaOH solution is concentrated by evaporation.

Properties : Sodium hydroxide is a white translucent solid. It is very deliquescent, i.e., it absorbs moisture from the air to form a solution. The sodium hydroxide readily absorbs carbon dioxide from air and becomes coated with a white layer of Na_2CO_3 . It is an ionic compound

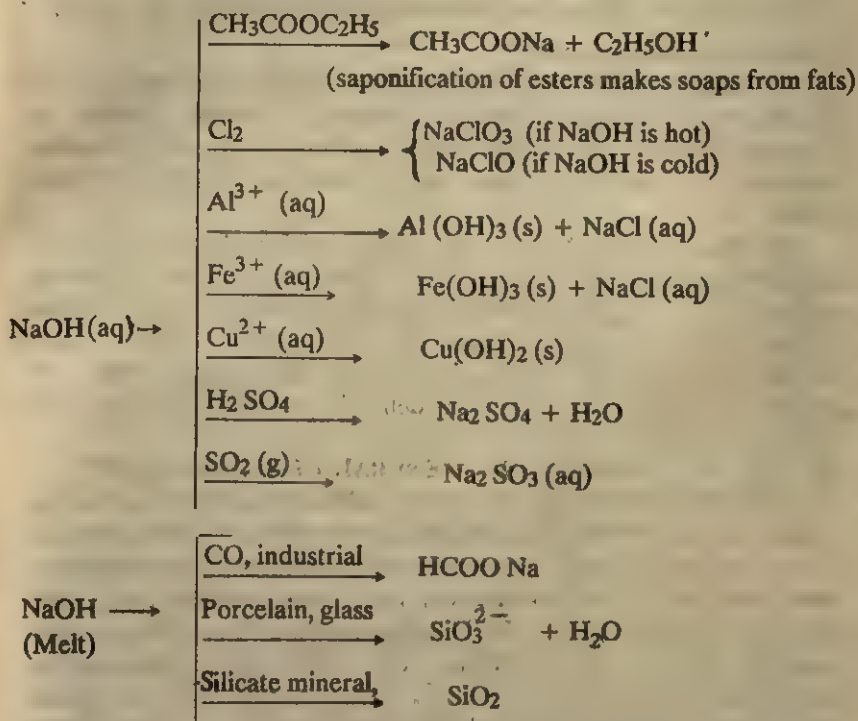
that melts and boils without decomposition. It melts at 591K. It readily dissolves in water with the evolution of a great deal of heat and yields strongly basic solution. Its solution also absorbs CO_2 from air forming sodium carbonate and water.



In its chemical reactions sodium hydroxide behaves as a typical alkali.

1. It neutralizes/reacts with (i) an acid forming a salt and water, (ii) acidic oxides forming salts, (iii) some salt solutions precipitating their hydroxides, and (iv) ammonium salts on heating and yields ammonia gas.

2. When fused, sodium hydroxide attacks silicate minerals and glass. Some of the important reactions of sodium hydroxide are given below,



Uses of Sodium Hydroxide : Sodium hydroxide is used extensively in the manufacture of chemicals, rayon, textiles, soap, dye, cleansers, paper and pulp. It is used in the purification of bauxite and in petroleum refining. The aqueous solution of sodium hydroxide is a valuable laboratory reagent and is used in titrimetric analysis. Chlorine, a by-product obtained in the manufacture of sodium hydroxide, is used in the production of PVC (polyvinyl chloride).

14.4.5 Potassium Chloride

Potassium chloride is an important source of potassium metal and all its compounds. The salt may be extracted from carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) by fractional crystallization as potassium chloride is less soluble at low temperature than magnesium chloride. The crude product is widely used in the manufacture of fertilizers. In fertilizer industry, potassium chloride and other salts KNO_3 and K_2SO_4 which are used in the production of fertilizers are called 'potash'. For this purpose, potassium salts are mainly obtained from sea water. A small plant has been set up in Kandala (Gujrat), where sea bitterns are used for the production of potassium chloride.

It is a colourless crystalline solid. It melts at 1063K and finally sublimes at 1773K. Large quantities of KCl are used in the manufacture of other potassium compounds such as hydroxide, nitrate, carbonate, etc.

14.4.6 Potassium Hydroxide

Potassium hydroxide or caustic potash, KOH is produced by the electrolysis of potassium chloride solution. Another method of preparing, KOH, which involves the treatment of aqueous potassium carbonate with slaked lime, has largely given way to the electrolytic method.

Potassium hydroxide is a white solid, which melts at 633K. It is highly deliquescent and absorbs CO_2 from the atmosphere forming carbonate. It is highly soluble in water and forms strongly alkaline solution (stronger than sodium hydroxide). It is highly corrosive in nature and destroys the organic tissues. It gives all such reactions which are possible with NaOH. Because of its deliquescent nature, it is used as a dehydrating agent.

14.5 GROUP 2 ELEMENTS – GENERAL CHARACTERISTICS

The metals beryllium, magnesium, calcium, strontium and barium belong to group 2 of the periodic table. They are close relatives of group 1. They are somewhat harder with higher melting and boiling points and are denser and less reactive (sodium reacts with water violently, magnesium reacts only with hot water). Their general pattern of reactivity is quite similar to that of group 1 elements. The general characteristics of the elements are summarized in Table 14.2. The elements have two electrons (ns^2) in the outermost shell, and thus, they form M^{2+} cations. These elements are less electropositive than alkali metals. As a group, they resemble the less electropositive metals of group 1 and the metal most resembling lithium turns out to be magnesium—the diagonal relationship.

As usual the behaviour of beryllium and its compounds is closer to that of aluminium than it is to that of other alkaline earth metals. This is again because of the significant difference in their sizes and electronegativity values. Except barium, all the metals in the group have close packed metallic structures at room temperature. Barium has body

centred cubic structure. Since they each have two valence electrons, they have stronger bonding and show higher cohesive properties than their group 1 neighbours. Thus they are harder. They have high conductivity values.

Trends in properties of the elements like atomic and ionic radii, density, electronegativity and ionization energy are as would be expected from their position in the periodic table (Table 14.2, Unit 5).

TABLE 14.2 : Properties of group 2 elements

Property	Be	Mg	Ca	Sr	Ba
Atomic number	4	12	20	38	56
Electron structure	[He]2s ²	(Ne)3s ²	[Ar]4s ²	[Kr]5s ²	[Xe]6s ²
Abundance in earth's crust (ppm)	6	20,900	36300	150	430
Atomic (metallic) radius, (pm)	112	160	197	215	222
Ionic radius, M ²⁺ (pm)	41	86	114	132	149
Melting point (K)	1560	922	1112	1041	1000
Boiling point (K)	3243	1378	1767	1654	1413
Density (g cm ⁻³) at 293K	1.85	1.74	1.55	2.63	3.62
Ionization energy, (kJ mol ⁻¹)	1st	737.5	589.6	549.2	502.7
	2nd	1750	1450	1060	960
Electronegativity	1.5	1.3	1.1	1.0	0.95
Electron affinity (kJ mol ⁻¹)	+100	+30	—	—	—
Reduction potential, E°(V)	-1.85	-2.37	-2.87	-2.89	-2.91
M ²⁺ (aq) + 2e ⁻ → M					

All except magnesium impart characteristic colours to the flame, Ca-brick red, Sr-crimson and Ba-apple green. Metals are reducing agents. Their strength as reducing agents (measured by redox potential) is shown by the vigour with which they reduce water and acids to hydrogen. These elements because of their reactive nature are found in combination as carbonates, sulphates and silicates.

The individual metals are named after minerals known long before their isolation. They were isolated by Humphry Davy in 1800 using electrolysis.

14.6 MAGNESIUM AND CALCIUM

Both magnesium and calcium belong to s-block elements with electron structure of the valence shell ns². They are denser and harder than the corresponding alkali metals in group 1 and have higher melting points. This shows the presence of stronger metallic and more compact lattice than group 1 metals. This also results in higher values of ionization energies for group 2 metals than group 1. The metals being powerful reducing agents cannot be isolated by reducing their oxides.

14.6.1 Occurrence

Magnesium and calcium do not occur in the native state. They are the most abundantly found elements in the earth's crust (magnesium and calcium occupy the sixth and third positions in the order of abundance).

This is one of the reasons why the group 2 elements are called earth metals. Minerals of magnesium are as follows :

Carbonates	Magnesite, MgCO_3 ; Dolomite $\text{CaCO}_3 \cdot \text{MgCO}_3$
Sulphates	Epsomite, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; Kieserite, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$
Chloride	Carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
Silicates	Olivine, $(\text{MgFe})_2 \text{SiO}_4$; Soapstone (talc), $\text{H}_2\text{Mg}(\text{SiO}_3)_2$ or $\text{Mg}_3 \text{Si}_4 \text{O}_{10} (\text{OH})_2$; Asbestos $\text{Ca}_2\text{Mg}_5 \text{Si}_8 \text{O}_{22} (\text{OH})_2$ or $\text{Mg}_3 \text{Si}_2 \text{O}_5 (\text{OH})_4$

Sea water contains an appreciable amount of magnesium chloride (0.13% Mg; 0.38% MgCl_2).

In India, magnesium is mainly found as dolomite and magnesite in Salem (Tamil Nadu) and Mysore.

Chlorophyll in green leaves of plants contain magnesium. Calcium is the most abundant s-block element. Vast quantities of calcium occur as the carbonates in chalk, limestone and marble. Other natural forms of calcium carbonate include, calcite, marine, shells, corals and pearls.

Smaller quantities of calcium occur as carbonate in dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$), as sulphate in anhydrite (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), as flouride in flourspar (CaF_2) and fluorapatite [$3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$] and as phosphate in phosphorite [$\text{Ca}_3(\text{PO}_4)_2$] and hydroxyapatite [$\text{Ca}_5(\text{PO}_4)_3 (\text{OH})$]. Sea water also contains some calcium salts in dissolved state. Calcium is vital for the growth of the plants and animals. Calcium carbonate and calcium phosphate are the building materials. Bones, teeth and horns are made of calcium phosphate. Shell of an egg is made of calcium carbonate.

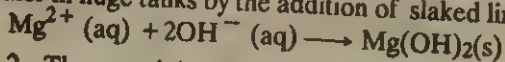
14.6.2 Isolation of Magnesium and Calcium

Magnesium : There are two common processes by which magnesium is produced ; (i) magnesium chloride is decomposed using electrolysis, and (ii) magnesium oxide is reduced to magnesium by silicon at very high temperatures.

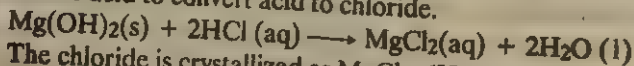
(i) By electrolysis

Much magnesium chloride for the electrolysis was earlier obtained from carnallite. It is now obtained from sea water which is an increasingly important source of raw materials :

1. To obtain the metal, magnesium hydroxide is precipitated from sea water in huge tanks by the addition of slaked lime, $\text{Ca}(\text{OH})_2$.

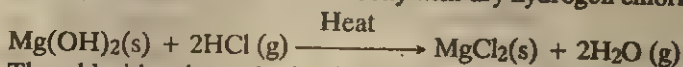


2. The precipitated hydroxide is separated and treated with hydrochloric acid to convert acid to chloride.



The chloride is crystallized as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

3. Now to obtain the fused magnesium chloride, the crystals of chloride are dehydrated by passing a current of dry hydrogen chloride gas. Mg(OH)_2 can also be treated directly with dry hydrogen chloride gas.

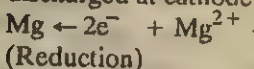


The chloride, thus, obtained is mixed with a molten mixture of sodium chloride and calcium chloride (temp. range 973-1023K). The molten mixture of MgCl_2 , NaCl and CaCl_2 is electrolysed in the Down's cell. Sodium chloride prevents the hydrolysis of MgCl_2 , lowers the melting point and increases the conductivity of the molten mass.

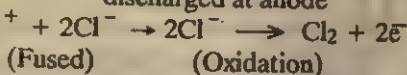
Electrolytic extraction is carried out in an atmosphere of coal gas to prevent the oxidation of molten magnesium.

The apparatus used is shown in Fig. 14.6. The following reactions take place within the cell :

Magnesium ions are discharged at cathode



Chloride ions are discharged at anode



Molten magnesium rises to the surface (less dense than the fused mass) and is removed from the cathode compartment with perforated ladles.

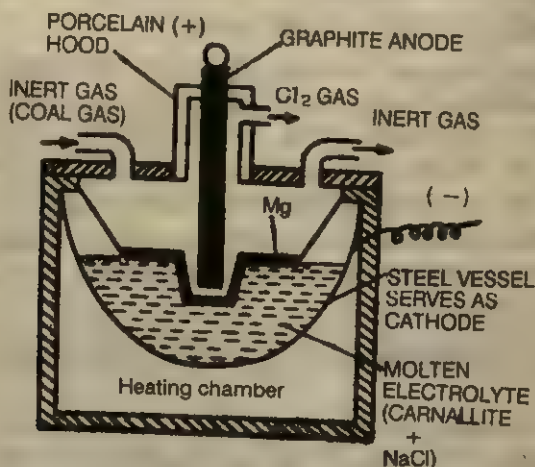
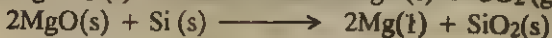
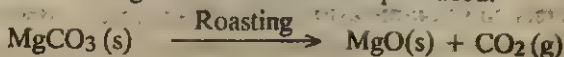


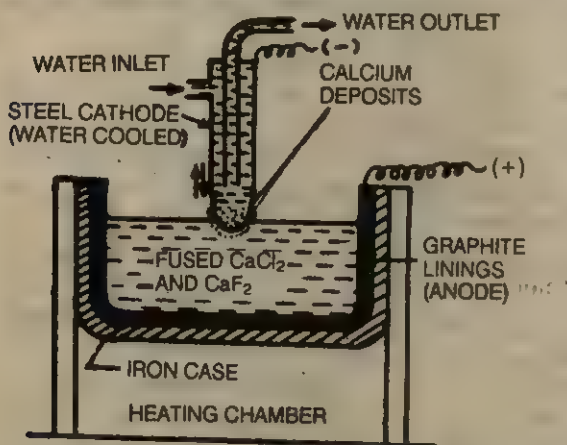
Fig. 14.6 : Electrolytic extraction of magnesium

(ii) By reduction with silicon

Magnesium ore is purified and is roasted in a furnace to make magnesium oxide which, in turn, is heated with silicon to high temperature. Magnesium and silica are produced.



Calcium : Calcium is commercially obtained by electrolytic dissociation of a fused mass of calcium chloride and calcium flouride (flux). The cell is illustrated in Fig. 14.7. The graphite body of the cell



serves as the anode. Calcium gets deposited around the tip of the steel cathode as it does not rise to the surface (calcium is not very light). As the time passes a thick continuous rod of calcium builds up around the cathode. The cathode used is movable. The movement of the cathode helps in the

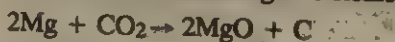
Fig. 14.7 Electrolytic extraction of calcium

deposition of calcium, forming long rods. With growth, the cathode is pulled up keeping up the cathode tip always under fused mass. This prevents melting of the metal and allows isolation in the solid form.

14.6.3 Properties of Magnesium and Calcium

Both magnesium and calcium are silvery white metals which are malleable and ductile at higher temperatures. Magnesium is the lightest of the widely used structural metals. The main reactions of magnesium and calcium (or alkaline earth metals) closely follow those of the alkali metals. Some of their typical reactions are included in Table 14.3.

Magnesium has such a strong affinity for oxygen that it burns in an atmosphere of CO_2 reducing it to elementary carbon.



14.6.4 : Uses of Magnesium and Calcium and their Compounds

Magnesium :

- (i) It is a useful metal because of its lightness. It is often alloyed with aluminium to make aircraft bodies. Its alloys with zinc, manganese and tin are also known. Some commonly used alloys and their uses are given in Table 14.5.
- (ii) Magnesium is used as a sacrificial anode to prevent iron from rusting.
- (iii) The intense white light of burning magnesium is used in military flares, flash light powders, distress signals and incendiary bombs.
- (iv) Its strong reducing nature is used in separating many metals and non-metals such as silicon and boron from their oxides.
- (v) A suspension of magnesium hydroxide in water (called

milk of magnesia) is used as an antacid when a person suffers from acute acidity. (vi) Magnesium carbonate forms a part of tooth-pastes.

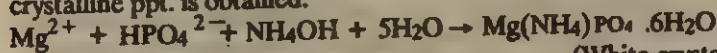
TABLE 14.3 : Reactions of magnesium and calcium

Reaction	Comments
1. $M + H_2 \xrightarrow{\text{Heat}} M^{2+} + 2H^-$ (M = Mg, Ca)	Magnesium reacts under pressure of H_2
2. $M + X_2 \longrightarrow M^{2+} + 2X^-$ (X = Halogens)	Proceed readily with all the halogens
3. $2M + O_2 \xrightarrow{\text{Heat}} 2MO$ (oxide)	Mg is not easily attacked by air due to the formation of a protective basic carbonate film on its surface. Peroxides and superoxides are obtained by other metals.
4. $M + S \xrightarrow{\text{Heat}} MS$	Mg reacts vigorously
5. $3M + N_2 \longrightarrow M_3N_2$ Nitride	Reactions are carried out at red heat
6. $M + 2C \xrightarrow{\text{Heat}} MC_2$ (Carbide)	Formed at very high temperatures, ionic in nature.
7. $M + 2H_2O \longrightarrow MC_2$ (Cold)	Mg does not react with cold water, but will react in steam.
8. $M + 2H^+ \longrightarrow M^{2+} + H_2$	Both the metals react readily displacing hydrogen.
9. $M + NH_3(l) \longrightarrow M^{2+}(NH_3) + 2e^-(NH_3)$	In gaseous ammonia, nitride is formed. Only Ca shows this reaction.

Calcium : (i) Calcium is used as a dehydrating agent for certain organic solvents ; as a reducing agent in the production of certain metals (thorium, uranium, etc.) ; as hardening agent for lead alloys used for covering cables ; making storage battery grids and bearings, etc. (ii) Because of its high reactivity towards oxygen and nitrogen, it is used for removing last traces of air and inert gases ; for removing residual gases in vacuum tubes and radio-valves. (iii) It is used as a deoxidizer in steel production. Its reducing nature also helps in removing sulphur from crude oil. (iv) Calcium compounds also have important uses. The uses of CaO , $CaSO_4$, $CaCO_3$ and $Ca(OH)_2$ will be given under individual compounds. Calcium phosphate on reacting with sulphuric acid forms an important fertilizer, calcium superphosphate, $Ca(H_2PO_4)_2$.

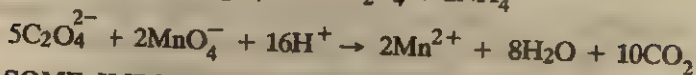
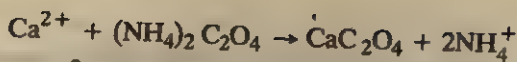
14.6.5 Detection Of Magnesium And Calcium.

Magnesium ions can be detected in its salts solution by adding disodium hydrogenphosphate, Na_2HPO_4 and ammonia solution. A white crystalline ppt. is obtained.



(White crystalline ppt.)

Calcium ion can be detected by the flame test (brick red flame). Ammonium oxalate reacts with its salt solution giving an insoluble ppt. of CaC_2O_4 , which can dissolve in dilute H_2SO_4 . This solution can decolourize a diluted solution of potassium permanganate.

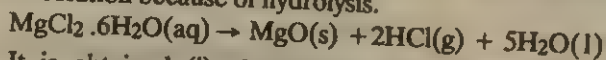


14.7 SOME IMPORTANT COMPOUNDS OF MAGNESIUM AND CALCIUM

Both magnesium and calcium form a large number of compounds. The compounds are generally ionic in nature. Compared to alkali metal compounds those of magnesium and calcium are not always readily soluble in water. Chloride and sulphate of magnesium; oxide, hydroxide, carbonate and sulphate of calcium will be discussed here.

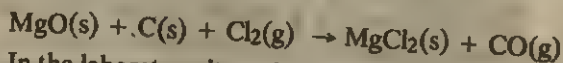
14.7.1 Magnesium Chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)

Magnesium chloride is mainly obtained from carnallite. Sea water is a good source of magnesium chloride. It crystallizes out from the aqueous solution on evaporation as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Anhydrous magnesium chloride cannot be prepared by direct evaporation of the aqueous solution because of hydrolysis.



It is obtained (i) by heating the hexahydrate in a current of hydrogen chloride (ii) by burning magnesium in chlorine or (iii) by carefully heating the double salt, $\text{NH}_4\text{Cl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

(Water and NH_4Cl are driven off). Generally it is formed by heating magnesium oxide mixed with carbon in the current of dry chlorine gas.



In the laboratory, it can be prepared by the reaction of hydrochloric acid on magnesium oxide or carbonate. It is a white crystalline deliquescent solid. It melts at 981K. Its solubility in water is 54.1 g/100 g at 293K.

Uses: Magnesium chloride finds use in the production of elemental magnesium and sorel's cement ($\text{MgCl}_2 + \text{MgO}$). It is used for lubricating threads in spinning, for preparing artificial stones. It helps in slating down the dust particles, and hence, sprinkled on the roads.

14.7.2 Magnesium Sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$)

Magnesium sulphate was first found to be present in spring water at Epsom, Surrey (U.K.) in 1695. The colourless crystalline heptahydrate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is known as Epsom salt. It also occurs as natural salt deposits; kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), and kainite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$). In the laboratory, it is prepared by the action of H_2SO_4 on magnesium metal, magnesium oxide (magnesia) or magnesium carbonate. On a commercial scale, it is prepared by the reaction of boiling sulphuric acid on dolomite (CaSO_4 , a sparingly soluble salt separates out) or by recrystallization of the naturally occurring salt.

Magnesium sulphate is a colourless, crystalline solid with a bitter taste. It loses six molecules of water at 423K. On further heating, it loses the last molecule of water and also decomposes partially evolving SO_3 . It decomposes forming oxide on strong heating.

Uses : Magnesium sulphate is used (i) in medicine as a purgative (mostly for veterinary purposes), (ii) as a mordant for cotton goods in the dyeing industry, and tanning industry (iii) for producing fire proof fabrics, (iv) as a laboratory reagent, and (vi) as platinized magnesium sulphate in the manufacture of H_2SO_4 . It has found its use in polishing powders and in heat insulation.

14.7.3 Calcium Oxide, CaO

Calcium oxide is the most common and important of all the calcium compounds. Its commercial name is quicklime or caustic lime.

Industrially calcium oxide is obtained by heating one of the forms of calcium carbonate, e.g. limestone to 1173-1473K in a lime kiln (Fig. 14.8).



The thermal decomposition is reversible and thus removal of carbon dioxide prevents its recombination with calcium oxide.

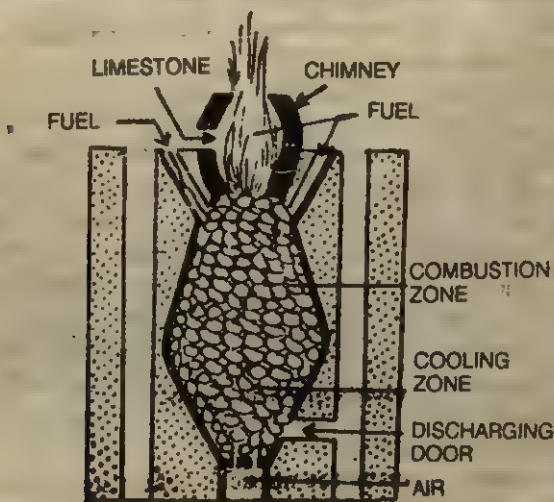


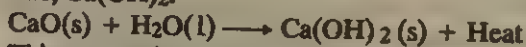
Fig. 14.8 : A view of the kiln for the manufacture of calcium oxide.

Limestone is added to the lime kiln through the hopper. Heat is provided by burning coal in fire boxes present on the sides of the kiln. Carbon dioxide and other waste gases escape through the openings near the top. Quicklime is collected from the bottom of kiln. This is a continuous process. Quicklime is usually obtained as white lumps.

In the laboratory, calcium oxide is best prepared by heating the nitrate or hydroxide.

Properties : Pure quicklime is a white porous solid. It melts at 2850K. It is extremely stable and does not decompose even on fusion. It gives brilliant white limelight, when heated to a high temperature.

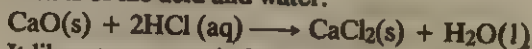
Quicklime reacts readily and violently with water at ordinary temperature (strong affinity for water). When quicklime is moistened with water, it combines with water producing a hissing sound and lot of heat. As the reaction proceeds, the mass swells and cracks, becoming very hot and steaming, finally crumbling to a fine white bulky powder. The fine powder obtained is called **slaked lime** and consists of calcium hydroxide, Ca(OH)_2 .



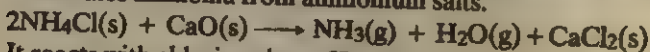
This process is called the **slaking of lime**.

In dry air, quicklime keeps indefinitely. On exposing to atmosphere for long, it absorbs moisture and carbon dioxide forming a mixture of calcium hydroxide and calcium carbonate.

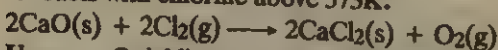
Calcium oxide is a basic oxide and dissolves in acids producing calcium salts of the acid and water.



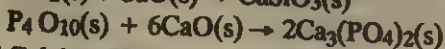
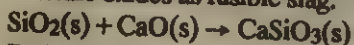
It liberates ammonia from ammonium salts.



It reacts with chlorine above 573K.

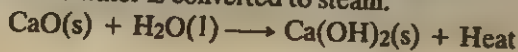


Uses : Quicklime has been put to various uses : (i) In the manufacture of slaked lime, cement, glass, bleaching powder, calcium carbide, basic calcium nitrate, calcium bisulphate, etc. (ii) Used in the paper making, tanning, as a fertilizer and in calcium-sand mortar, (iii) Used in the manufacture of sodalime by slaking quicklime with concentrated aqueous caustic soda. (iv) Used in laboratory as an absorbent for carbon dioxide and waste acidic gases and for decarboxylation of salts of carboxylic acids. (v) Used to dry ammonia and sometimes to dry alcohol. (vi) In the purification of coal gas and softening of water. (vii) Used in metallurgical processes (as lining in furnaces) to remove acidic oxides as fusible slag.



14.7.4 Calcium Hydroxide, Ca(OH)_2

Calcium hydroxide is commonly known as slaked lime or hydrated lime. Calcium hydroxide is produced commercially by the action (shaking of lime) of cold water on quicklime. On adding water to a lump of quicklime, the lump begins to swell and break up. It gets very hot and some of the water is converted to steam.



It can also be prepared by the action of water on calcium metal.

A suspension of slaked lime in water is called **milk of lime** and is used as a cheap industrial alkali. The filtered saturated solution is called **lime water** which is used for testing carbon dioxide.

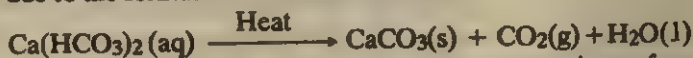
Properties : Calcium hydroxide is a white amorphous powder. It is slightly soluble in water and its solubility falls with increase in temperature. On heating to red heat, it rapidly evolves steam, leaving quicklime. When carbon dioxide is passed through the saturated solution of calcium hydroxide (lime water), it first turns milky due to the formation of calcium carbonate.



On passing CO_2 for long, the solution again becomes clear. Here excess of carbon dioxide redissolves calcium carbonate forming calcium bicarbonate, $\text{Ca(HCO}_3)_2$.



This reaction also accounts for the presence of temporary hardness in water. When the solution of bicarbonate is heated, it acquires milky appearance again due to the formation of calcium carbonate.



On passing chlorine through a cold suspension of calcium hydroxide (milk of lime), calcium oxychloride CaOCl_2 (bleaching powder) is formed.



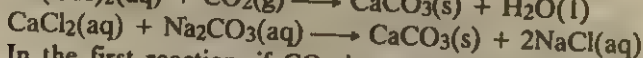
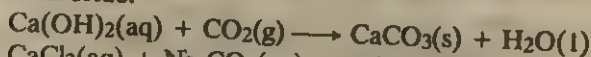
Uses : Calcium hydroxide is used : (i) In the chemical industry, in paper making, in tanning, as a fertilizer and in lime-sand mortar. (ii) In the manufacture of glass, bleaching powder, caustic soda, etc. (iii) For the absorption of acidic gases, in the purification of coal-gas, in the recovery of ammonia from waste liquors (ammonium chloride) in the ammonia-soda process (Solvay process) and the softening of water. (iv) In white-washing. After applying, slow absorption of carbon dioxide occurs with the formation of calcium carbonate which on drying gives a bright appearance to the surface. (v) In the form of lime water in medicine as a dressing of burns and as an antidote for poisoning by sulphuric or oxalic acid, to correct the acidity of soil and to make heavy soils lighter.

14.7.5 Calcium Carbonate, CaCO_3

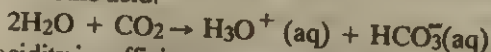
Both magnesium and calcium carbonates occur naturally. Limestone occurs in our country at a number of places : Birmatrapur (Orissa), Jabalpur (Madhya Pradesh), Rajasthan, Dehradun (UP). Because of their insolubility in water, they may be prepared by precipitation and are the most important minerals of these elements. Limestone and marble are two well known forms. Calcium carbonate crystallizes in two forms ; the stable calcite (hexagonal system) and the metastable aragonite (rhombohedral system). Calcite is the usual form and is

found under various names : iceland spar is composed of colourless crystals ; marble and limestone are aggregates of interlocking crystals ; chalk, microcrystalline in nature, is a product from the shells of dead marine creatures. Aragonite occurs in coral and the shells of molluscs.

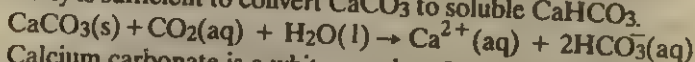
Commercially, calcium carbonate is prepared by passing carbon dioxide through slaked lime or by the addition of sodium carbonate to calcium chloride.



In the first reaction, if CO_2 is passed for long, CaCO_3 dissolves forming calcium bicarbonate. This is because, CO_2 on dissolving in water gives carbonic acid.



This acidity is sufficient to convert CaCO_3 to soluble CaHCO_3 .



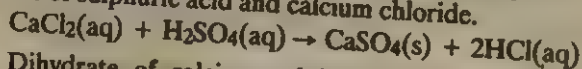
Calcium carbonate is a white powder. It decomposes when heated, giving the oxide and CO_2 .



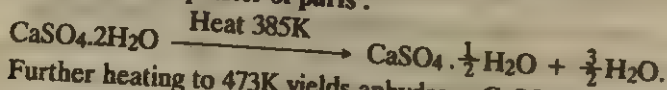
Uses : Calcium carbonate is used widely as the source of quicklime and in the manufacture of cement. Pearls (built up of concentric layers of calcium carbonate) are used in jewellery. It finds its use as flux in metallurgical extraction of metals *e.g.* iron, *etc.* In building constructions, it is used in the form of marble, mortar and cement. It is used as an important laboratory reagent (*e.g.* in the preparation of CO_2 gas). It is also used in the ammonia soda process (Solvay process) and in the glass industry.

14.7.6 Calcium Sulphate, CaSO_4

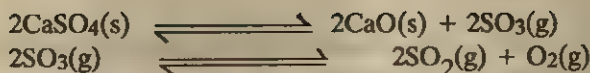
Anhydrous calcium sulphate occurs in nature as the mineral anhydrite, CaSO_4 and as the dihydrate gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Enormous deposits of gypsum are available. Punjab and Rajasthan are rich in these deposits. Gypsum exists in various forms : selenite (transparent) satin spar (fibrous) and alabaster (opaque). It is sparingly soluble in water, and hence, may be prepared in the laboratory by precipitation, *e.g.*, by mixing solutions of sulphuric acid and calcium chloride.



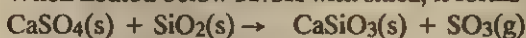
Dihydrate of calcium sulphate on heating at 385K loses three quarters of its water of crystallization, giving a white powder of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, which is called 'plaster of paris'.



Further heating to 473K yields anhydrous CaSO_4 which can absorb water but stronger heating above 673K gives a 'dead burnt plaster' which does not set when mixed with water. Above 1233K, it dissociates.



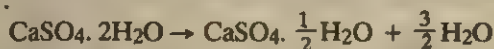
When heated below 1173K with silica, it forms silicate.



Uses : Gypsum has been put to various uses, e.g., in the manufacture of plaster of paris, ammonium sulphate (a fertilizer; at Sindri, gypsum is used for manufacturing fertilizer, Unit 12), Portland cement, blackboard crayon (chalk), plate glass, terracota, pottery, glazed paper and sulphuric acid.

14.7.7 Plaster of Paris, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$

The hemi-hydrate of calcium sulphate is known as 'plaster of paris'. It is prepared by heating gypsum (natural source of calcium : $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) at 385K. At this temperature, gypsum loses $\frac{3}{4}$ th of its water.



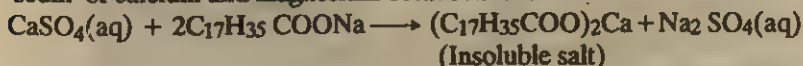
At higher temperature, the anhydrous salt is formed. This is known as dead burnt plaster.

Plaster of paris is a white powder. It absorbs water at ordinary temperature with evolution of heat. It has a distinct property of setting up on wetting with water. On mixing with water it sets to hard solid, which consists of a mass of interlocking crystals of the dihydrate. The formation of dihydrate coupled with expansion is an important property for making plaster casts.

Uses : Plaster of paris finds uses as follows : (i) In making casts and patterns for moulds and statues. (ii) Used in surgery for immobilising fractured parts of the body, e.g., orthopedic and dental plasters. (iii) Used for preparing blackboard chalks. (iv) Used as fire proofing material. (v) Used in the manufacture of wall boards, made by the hydration of mixture of lime and plaster of paris often with fibre base. (vi) Used for making decorative materials. Its major amount is used in the building industry and as a component of the plaster used for the surface of interior walls and ceilings.

14.8 HARD AND SOFT WATER – WATER SOFTENING

Hard water does not give lather with soap. Dissolved salts of Ca^{2+} , Mg^{2+} and Fe^{2+} contribute to hardness in ground water. These are found to be associated with bicarbonate, chloride and sulphate ions. A soap such as sodium octadecanoate, $\text{C}_{17}\text{H}_{35}\text{COONa}$ (sodium salt of fatty acid) reacts with calcium and magnesium ions to form an insoluble 'scum' of calcium and magnesium octadecanoate.



Only when sufficient soap has been added to precipitate calcium and magnesium ions, the soap will lather. Detergents do not form scum in

hard water. They are the sodium salts of sulphonic acids and their calcium and magnesium salts are soluble in water.

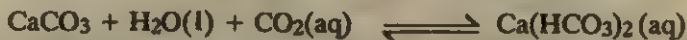


Sodium dodecylbenzene sulphonate (a detergent)

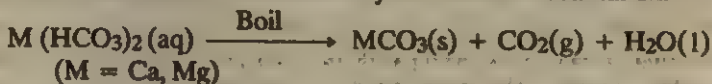
Deposits of scale and fur are seen in pipes, boilers, kettles as a result of heating hard water. It is healthier to drink hard water. There is more heart diseases in soft water areas. Better beer is brewed in hard water areas. There are two types of hardness in water; temporary and permanent.

Temporary hardness

Cause : The soluble hydrogencarbonate salts, produced by the action of dilute carbonic acid on rock, make water hard. Limestone (rock) reacts with rain water that contain dissolved carbon dioxide.



Cure : Boil the water. Boiling decomposes the hydrogencarbonates to carbon dioxide and insoluble carbonates. Carbon dioxide is driven off. Insoluble carbonates can be removed by filtration or decantation.



Temporary hardness can also be removed by the addition of a calculated amount of lime when magnesium and/or calcium carbonate is precipitated - "Add lime to remove lime".

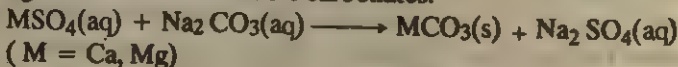


(M = Ca, Mg)

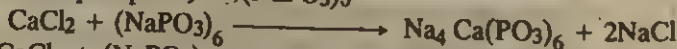
Permanent hardness

Cause : The soluble sulphates or chlorides of magnesium, calcium and iron (II) make water hard. Rocks containing these salts are soluble in rain water.

Cure : Permanent hardness cannot be removed by boiling the water. (1) Washing soda, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ is added to precipitate calcium and magnesium ions as insoluble carbonates.



(2) Hardness can also be removed by adding calgon, a sodium salt of hexametaphosphate, i.e., $(\text{NaPO}_3)_6$

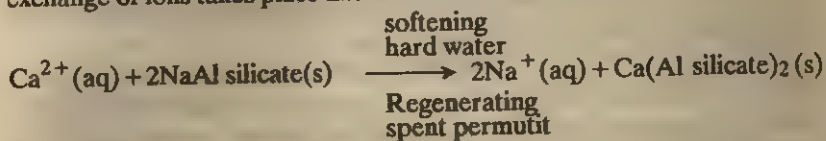


The calcium or magnesium polymetaphosphates formed remains in solution, but does not react with soap readily as the ions are complexed.

The softening of hard water is often accomplished by a process called 'ion exchange'. Both naturally occurring sodium aluminosilicates known as 'Zeolites' and 'synthetic resins' are used as exchangers.

(3) Ion exchangers

When hard water is passed slowly through a column containing sodium aluminium silicate (Zeolite; trade name 'PERMUTIT') an exchange of ions takes place and the water is softened.



(M = Ca, Mg; Z = anion of zeolite)

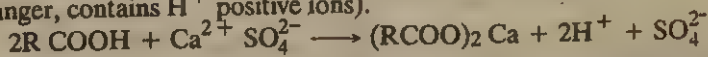
Constant use of Permutit makes it ineffective because all the sodiums ions are replaced by calcium and magnesium ions. At this stage it requires regeneration. This is done by passing through it concentrated solution of sodium chloride.

Another class of materials which are employed for water softening are called organic exchange resins.

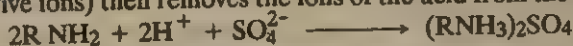
Synthetic Resin Ion-Exchangers have been developed which remove both cations (positive ions) and anions (negative ions) from hard water, i.e., they demineralize the water completely. Amberlite and zeocarb belong to this class of resins.

These resins are mainly made of hydrocarbon chain of high molecular mass and are covalently bonded to negatively charged groups such as SO_3^{2-} or positively charged groups of the type NR_3^{+} . Thus the former type of resin is capable of exchanging cations and the latter can exchange its anions.

When water passes through a resin-bed, the Ca^{2+} , Mg^{2+} or Fe^{2+} become attached to and displace hydrogen ions in the resin (cation exchanger, contains H^{+} positive ions).



The latter type of the resin (anion exchanger, contains OH^{-} negative ions) then removes the ions of the acid from the water.



In this, all the ions from the water can be removed, and thus, a deionized water can be obtained. The used cation and anion exchange resins are regenerated by reversing the process and washing them with a concentrated solution of an acid or a base.

In recent years, the use of ion exchangers in the treatment of water for industrial and domestic purposes has grown tremendously.

14.9 GROUP 13 ELEMENTS – GENERAL CHARACTERISTICS

Group 13 of the periodic table contains boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl). Within the group, there is a great variation in basicity. Boron is a nonmetal which has already been discussed in Unit 12, and the other elements in the group are metals. There is a distinct difference in properties between boron and the other elements. Their valence shell electron structure is ns^2, np^1 and generally form compounds with +3 oxidation state..

As seen with s – block elements, boron behaves differently from the other members of the group (reasons already discussed in Unit 12). These elements have smaller atomic radii and higher ionization energies as compared to s-block elements of the same period. Their atomic radii and densities show a general increase while boiling points and ionization energies (Table 14.4) experience a fall in value. The difference in the properties of boron and aluminium on the one hand and of both of them from the rest of the members of the group is due to the electronic structure of the penultimate shell.

TABLE 14.4 : Properties of group 13 elements

Property	B	Al	Ga	In	Tl
Atomic number	5	13	31	49	81
Electronic structure	(He) $2s^2 2p^1$	(Ne) $3s^2 3p^1$	(Ar) $3d^{10} 4s^2 4p^1$	(Kr) $4d^{10} 5s^2 5p^1$	(Xe) $4f^{14} 5d^{10} 6s^2 6p^1$
Abundance in earth's crust (ppm)	10	81300	15	1	0.3
Atomic radius, (pm)	98	143	141	166	171
Covalent radius, (pm)	82	125	125	144	155
Ionic radius, M^{3+} (pm)	20	50	62	81	95
Melting point (K)	2573	933	303	429	576
Boiling point (K)	2823	2740	2676	2273	1730
Density (g/cm^3) at 293K	2.34	2.7	5.91	7.3	11.8
Ionization potential, (kJ mol^{-1})	1st	800	577	579	589
	2nd	2427	1816	1979	1820
	3rd	3658	2745	2962	2703
Electronegativity	2.0	1.45	1.8	1.5	1.45
Electron affinity (kJ mol^{-1})	-23	-50	—	—	—
Reduction potential E° (V)					
$M^{3+} + 3e^- \rightarrow M$	-0.87	-1.66	-0.56	-0.34	+1.26
$M^+ + e^- \rightarrow M$	—	0.55	-0.79	-0.18	-0.34
			Acid		
			-1.39		
			(Alkali)		
Oxidation state	-3 to +3	+3	+1, +3	+1, +3	+1, +3

The soft, light and very malleable metals (except boron) are widely distributed in nature but only aluminium is abundant.

14.10 ALUMINIUM

Aluminium, the most important element in group 13, belongs to p-block elements. It was discovered by H.C. Oestred, the Danish scientist, in 1825. Aluminium is a typical metal; although some of its compounds (e.g. the halides and oxides) have properties which are borderline between those of metals and non-metals. It is not a very reactive metal than would be suggested by its redox potential because of the formation of a coherent protective coating of oxide on its surface. It tends to form more covalent compounds as indicated by its high ionization energy values.

14.10.1 Occurrence

Aluminium is the third most abundant element (after oxygen and silicon) in the earth's crust and it is the most abundant (8.3% by mass) of all the metals. It is not found free in nature. Its important ore is bauxite (hydrated aluminium oxide, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) from which the metal is obtained electrolytically. Another important ore is cryolite, Na_3AlF_6 . Aluminium is a major constituent of igneous minerals including complex aluminium silicates like feldspar (KAlSi_3O_8) and mica [$\text{KAlSi}_3\text{O}_{10}(\text{OH})_2$]. These, in turn, weather in temperate climates to give clay mineral such as kaolinite [$\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$]. A small amount of aluminium is also found in minerals like spinel (MgAl_2O_4), garnet [$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$] and beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$). Anhydrous aluminium oxide occurs as corundum, ruby and sapphire. Emery is a mixture of Al_2O_3 and Fe_3O_4 .

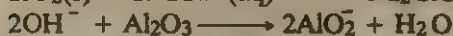
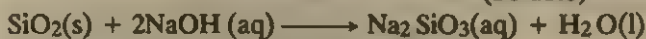
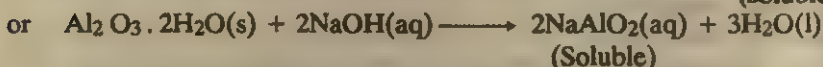
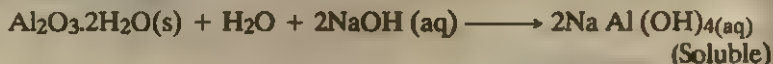
Aluminium occurs extensively as bauxite in Sambalpur and Korapur districts of Orissa, Chota Nagpur, Madras, Jabalpur and Rewa. It is also found in Katni, Belgaum and a place near Jammu. India is the largest supplier of mica. Bihar, Madhya Pradesh, Maharashtra, Tamil Nadu and Jammu & Kashmir are very rich in mica deposits.

An aluminium smelter has been set up at Hirakund for producing aluminium ingot. At BALCO (Bharat Aluminium Company Ltd., Korba) and in other industries, bauxite is the chief source of aluminium.

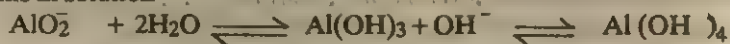
14.10.2 Isolation of Aluminium

The extraction of aluminium from bauxite involves two steps. First bauxite is purified and then electrolysis of molten alumina is carried out to produce aluminium metal. Bauxite is a mixture of hydrated oxides of aluminium and iron. Silica and clay are also associated with them. Pure aluminium oxide is obtained by the leaching process from the ore by utilising the fact that it is amphoteric, whereas the impurities, silicon dioxide is acidic and ferric oxide is basic. The ground ore is treated as suggested here. The ore is treated with hot sodium hydroxide solution. Because of the amphoteric nature of the aluminium ion (aluminium oxide is amphoteric-soluble both in strong acids and strong bases) the alumina is dissolved away as aluminates from the ore impurities while iron Fe_2O_3

a basic metallic oxide, insoluble in strong bases) and other impurities remain undissolved and are filtered off. It has been suggested that in the course of reaction, initially aluminium hydroxide is formed which dissolves in excess of sodium hydroxide to form soluble sodium aluminate, NaAl(OH)_4 . The sodium aluminate is unstable in nature and gets changed into metaaluminate (NaAlO_2) while the reaction is still in progress. Silica, an acidic impurity, dissolves in sodium hydroxide and forms sodium silicate.



The solution of metaaluminate is diluted to the extent that hydrolysis occurs giving a precipitate of Al(OH)_3 . Sodium silicate remains in solution.



This reaction is reversible. To precipitate Al(OH)_3 completely, it is necessary to remove OH^- ions. This is accomplished by passing CO_2 gas which on reacting with water produces carbonic acid (unstable). Carbonic acid on decomposition supplies H^+ ions. H^+ ions so formed reduce the OH^- ions concentration effectively giving the desired products. Sometimes a little freshly precipitated Al(OH)_3 is added for seeding to the filtrate when most of the metal from the solution is precipitated as Al(OH)_3 . This precipitate is heated to 1470K to obtain anhydrous alumina.



This method of purification is known as Baeyer's process and is illustrated through Fig. 14.9.

Now the purified molten Al_2O_3 is subjected to electrolysis in Hall's cell (Fig. 14.10) at 1200–1250K. Since the melting temperature of Al_2O_3 (2325K) is so high that electrolysis of the molten oxide cannot be accomplished, pure Al_2O_3 is dissolved in molten cryolite (increases the conductivity) which has much lower melting temperature than oxide. Calcium fluoride is also added to lower the temperature of the melt. Aluminium is discharged at the carbon lining of the cell which acts as the cathode. The molten aluminium collects at the bottom of the cell and is removed periodically. Oxygen is evolved at the anodes. A series of carbon electrodes dipped into the electrolyte serve as anodes. A part of the oxygen escapes and rest of it oxidizes the carbon anodes, which are slowly eroded.

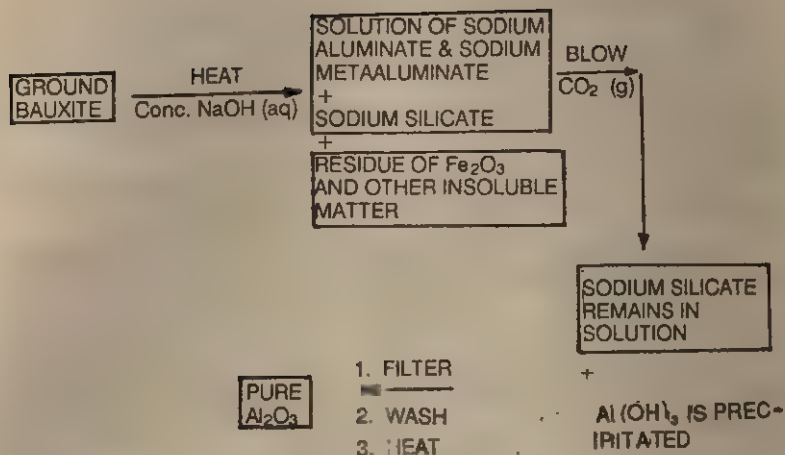


Fig.14.9. The recovery of pure aluminium oxide from bauxite.

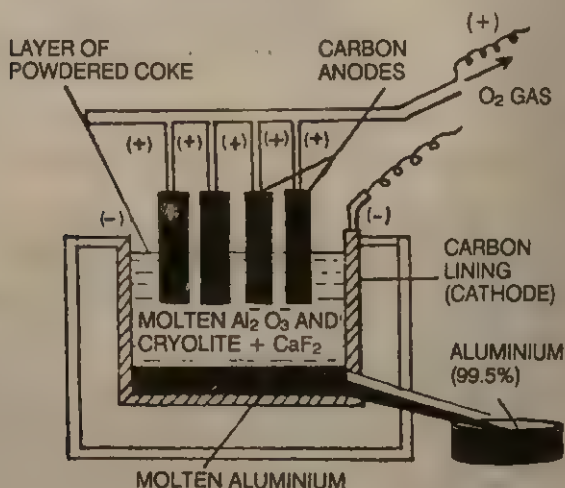
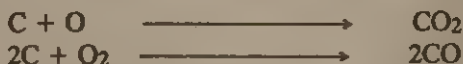


Fig. 14.10 The electrolytic manufacture of aluminium from purified aluminium oxide.



It is postulated that the equilibrium
 $\text{Al}_2\text{O}_3 \rightleftharpoons \text{Al}^{3+} + \text{AlO}_3^{3-}$
 (Fused)

gives rise to the electrode processes.

At the cathode: $\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$

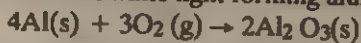


The aluminium obtained is of 99.5% purity. If necessary, it can further be purified by electrolytic refining process (Unit 2).

14.10.3 Properties of Aluminium

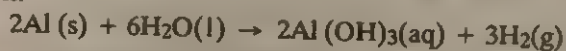
Aluminium is a soft and silvery-white metal of low density. It is a good conductor of heat and electricity. It is a reactive metal

(i) **Action of air :** Aluminium on heating in air or oxygen burns with a brilliant white light forming aluminium oxide.



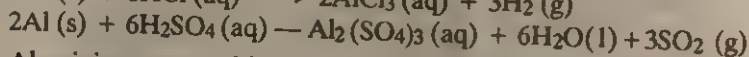
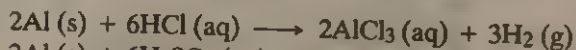
At ordinary temperature, a thin layer of oxide is formed on its surface. This protects it from further atmospheric corrosion and makes it less reactive. The oxide layer is non-porous to water, and hence, the metal is protected from further oxidation.

(ii) **Reaction with water :** Aluminium (free from protective layer of oxide) reacts with boiling water energetically displacing dihydrogen from it.



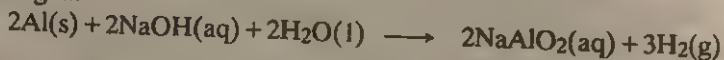
Saline water (e.g. sea water) corrodes it rapidly especially when it is hot.

(iii) **Reaction with acids :** Hydrochloric acid and dilute sulphuric acid, particularly when hot and fairly concentrated, react with aluminium to form salts.



Aluminium reacts with dilute nitric acid at normal temperature and does not react with conc. nitric acid. Nitric acid makes it passive by increasing the thickness of the oxide film.

(iv) **Reaction with alkalis :** Hot and concentrated caustic alkalis react with aluminium to form soluble meta-aluminate with the evolution of hydrogen.



Sodium metaaluminate

(v) **Reaction with metal oxides :** Aluminium reacts with metal oxides on heating. Iron scale (oxide) on reacting with aluminium is reduced to iron (Fig. 14.11)



Chromium and manganese oxides are also reduced to metals.

(vi) **Reaction with non-metallic elements :** Aluminium reacts with sulphur, nitrogen, carbon (at high temperature) and the halogens to form compounds, Al_2S_3 , AlN , Al_4C_3 and AlX_3 .

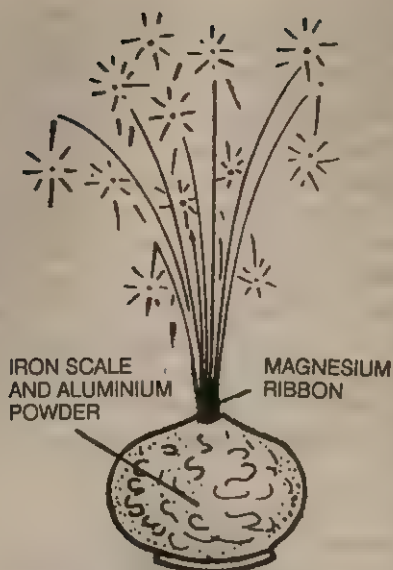


Fig. 14.11. Splashing of white-hot sparks of burning reduced iron
14.10.4 Uses of Aluminium

The important applications of aluminium are connected with its low density, strength and stability of alloys to air and water. Some are listed below :

(i) Since aluminium is a good conductor of heat and electricity, resists corrosion and light, it is widely used in transmission cables, household utensils and laboratory apparatus.

(ii) Since aluminium is an excellent reflector of light and heat, it is used for silvering mirrors. The polished surface of aluminium finds its use in the reflectors of car headlights. Fire fighting suits coated with aluminium protect the fire fighters from the fire and keep them cool. Newly born babies are sometimes wrapped in aluminium foil which keeps them warm by reflecting heat lost from body.

(iii) Aluminium and its alloys are used extensively as building materials, and for the construction of aeroplanes, small boats, railways coaches and ships. Automobile industries are the good consumers of aluminium alloys. Many parts of cars. *e.g.* engine blocks, piston heads, *etc.* are made of aluminium.

(iv) Being non-toxic, aluminium foil is used for packing food-materials.

(v) Finely divided aluminium powder mixed with mineral oil is used in silvery paint and lacquers. Containers used for storing petroleum products are generally silver painted to reflect the heat.

(vi) Dyed anodized aluminium is used for door and window frames, utensils for storage purposes, electrical lamps and other aluminium articles.

(vii) It finds use in the extraction of chromium and manganese. Aluminium powder is used in aluminothermy. This process is used in joining broken pieces of iron rails (girder), machine parts, etc.

Aluminothermy is the reduction process by aluminium of the oxide of a less reactive metals. In this process, a mixture of aluminium powder (3 parts) and iron oxide (one part) is taken in a crucible with a hole at the bottom (Fig.14.12). The mixture, known as thermite mixture, is covered with a ignition mixture ($\text{Mg} + \text{BaO}_2$). The magnesium ribbon is inserted into the ignition mixture and lit. When the flame reaches the ignition mixture sufficient heat is evolved to start a reaction between aluminium and iron oxide. The reaction is exothermic, and such a high temperature is reached that iron produced during the reaction melts and is allowed to drop over the gap in the broken girder which is kept hot. The molten iron fills the gap and joins the broken girder on cooling.

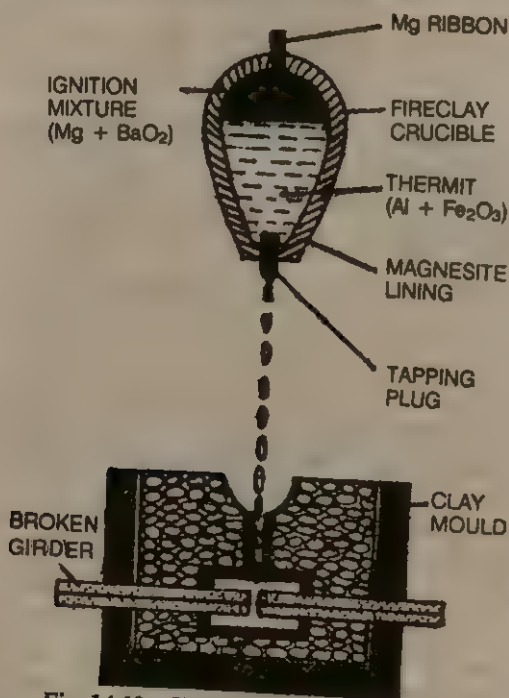


Fig. 14.12: Welding by aluminothermy

14.10.5 Alloys

Aluminium alloys are used widely because they are corrosion resistant (stable to air and water) and have a high tensile strength. Some commonly used alloys and their uses are given in Table 14.5. To increase resistance to corrosion, the alloys are coated with a thin film of oxide. This coating is done electrolytically. They are called Alclads or Aldurals. Anodized aluminium and its alloys are used extensively.

TABLE 14.5 Aluminium alloys and their uses

Alloy	Composition	Properties	Uses
Duralumin	Al 95% Cu 4% Mg 0.5% Mn 0.5%	Light, weight, hard, strong, resistant to corrosion	For the construction of aeroplanes, boats, tubes, cables and rivets.
Magnalium	Al 70–95%, Mg 30–5%	Light weight hard, strong	For making machine parts, balances household appliances etc.
Alnico	Al 12%, Fe 63% Ni 20%, Co 5%	Highly magnetic	For making permanent magnets
Aluminium bronze	Al 2–10% Cu 98–90%	Golden yellow in colour	For making imitation jewellery, coins, utensils, paints, statues, machinery castings, etc.
Dowmetal	Al 8–5%, Mn 0.5% Cu 2% Ca 0.5% Mg 87.85%	Light	For making machine parts, etc.

14.11 SOME IMPORTANT COMPOUNDS OF ALUMINIUM

Aluminium forms a large number of compounds. In this section, we will study the halides and sulphates of aluminium.

14.11.1 Aluminium Halides

Aluminium forms both monohalides (AlX) and trihalides (AlX₃). Monohalides are gaseous in nature and are short lived. Table 14.6 shows a comparison of some properties of the aluminium halides.

TABLE 14.6 : A comparison of aluminium trihalides

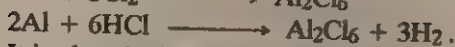
Property	AlI ₃	AlCl ₃	AlBr ₃	AlF ₃
Melting point (K)	1563	466	370.5	462.4
Boiling point (K)	Sublimes above m p	Sublimes at 453K	528	654
Heat of formation ΔH_f (kJmol ⁻¹)	1498	707	527	310
Condition for hydrolysis	Steam	Water	Water	Water
Solubility in water	Insoluble	Readily soluble	Readily soluble	Readily soluble
Solubility in organic solvent	Soluble	Soluble	Soluble	Soluble

The distinct change in the properties from fluoride to iodide is because of ionic nature of fluoride to covalent structures (triiodide is typically covalent).

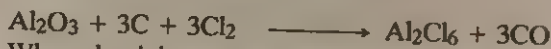
AlF₃ is produced by treating Al₂O₃ with HF gas at 473K and the other trihalides are made by the direct exothermic combination of the elements.



Anhydrous aluminium chloride is prepared by passing dry chlorine or HCl gas over the heated aluminium powder.



It is also obtained when purified bauxite is treated with carbon and chlorine.



When aluminium metal is treated with strong hydrochloric acid and the solution is evaporated, crystals of hexahydrate, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ are formed.

Anhydrous aluminium chloride is a white crystalline solid soluble in organic solvents. It is very hygroscopic, absorbs water from the atmosphere and finally dissolves in water. Solid aluminium chloride is an ionic solid consisting of Al^{3+} and Cl^- ions.

Measurement of its density indicates its dimeric nature in the vapour phase and its formula should be written as Al_2Cl_6 .

The structure of aluminium chloride changes with temperature (Fig. 14.13). In the dimeric structure each aluminium acquires a lone pair of electrons from one chlorine atom of each monomeric covalent molecule, and thus two chlorine bridges are formed.

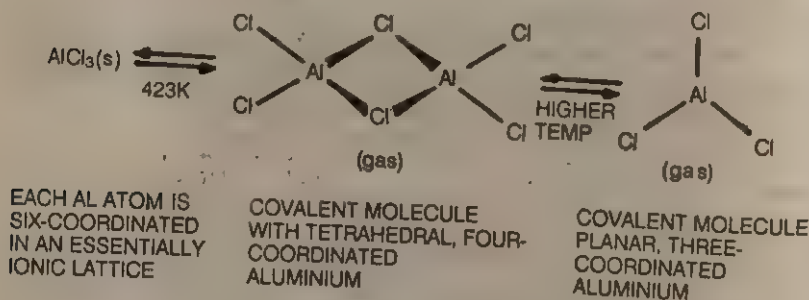


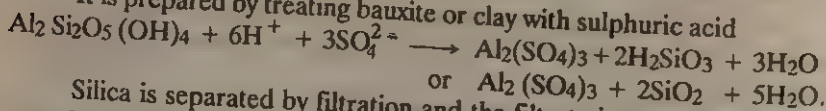
Fig. 14.13 Effect of heat on Al_2Cl_6

The AlX_3 structures (trigonal sp^2 hybridized) have a vacant orbital and are Lewis acids and adducts with Lewis bases $\text{H}_3\text{N} \cdots \text{AlCl}_3$.

Anhydrous aluminium chloride is used as a catalyst in the Friedel Craft's reaction. It is used in petroleum cracking and in the manufacture of dyes, drugs and perfumes.

14.11.2 Aluminium Sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$

It is prepared by treating bauxite or clay with sulphuric acid



Silica is separated by filtration and the filtrate is evaporated to get crystals. It is a colourless crystalline solid substance soluble in water. If strongly heated upto 1033K, the sulphate loses first water of

crystallization and finally SO_3 . Its aqueous solution is acidic due to hydrolysis. It forms many double salts with sulphates of other metals. These are called 'ALUMS'; their general formula is $\text{M}_2^{\text{I}}\text{SO}_4 \cdot \text{M}_2^{\text{III}}(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (where $\text{M}^{\text{I}} = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{NH}_4^+$ etc; $\text{M}^{\text{III}} = \text{Al}^{3+}, \text{Fe}^{3+}, \text{Cr}^{3+}$, etc.) Some commonly used alums of $\text{Al}_2(\text{SO}_4)_3$ are :

Potash alum $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$.
Sodium alum $\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

Alums are extensively used for softening and purifying water and as mordants in dyeing. They act as styptics on small cuts. Aluminium sulphate is used : (i) in printing and dyeing industry, (ii) in the sizing of paper, (iii) in the water proofing of fabrics and dyeing of fabrics, (iv) in tanning leather, and (v) in the foamite fire extinguisher. Sulphate being the cheapest soluble salt of aluminium, is used as a source of aluminium hydroxide for the purification of water.

14.12 CEMENT

Cement is a very important building material. In 1824 an Englishman, Joseph Apsdin, a mason of Leeds, discovered that when a strongly heated mixture of limestone and clay was mixed with water and allowed to stand, set to a hard mass which resembled a famous building stone, 'Portland rock' of England. He called this artificial material 'Portland cement'.

In India, the cement was first manufactured in Madras (Tamil Nadu) in 1904. The Indian Cement Co. Ltd. started manufacturing cement at Porbandar, Kathiawar in 1914. Thereafter the cement industry had its steady and rapid progress. Today, there are about 100 cement factories in our country. The production of cement in these factories is very high (~ 369 lakh tonnes per annum). India now exports cement,

The average composition of portland cement is as given below :

Lime (CaO)	62%	Silica (SiO_2)	22%
Alumina (Al_2O_3)	7%	Iron Oxide (Fe_2O_3)	3.5%
Magnesia (MgO)	2.5%	Alkali oxides	1.5%
Sulphur trioxide	1.5%		

Manufacture of Cement

There are two methods for the manufacture of Portland cement – the wet process and the dry process.

In the wet process, the raw materials, limestone and clay are first crushed in crushers, mixed in proper proportions and then the mixture is finely ground and homogenized. The fine mixture is converted to slurry by adding a little water.

In the dry process, the powdered raw materials are mixed in proper proportions and then pulverized to further fineness.

A rotary kiln, about 50 metres long and 2 to 6 metres in diameter is used for heating. It is made of steel sheet and is lined inside with firebricks (Fig. 14.14).

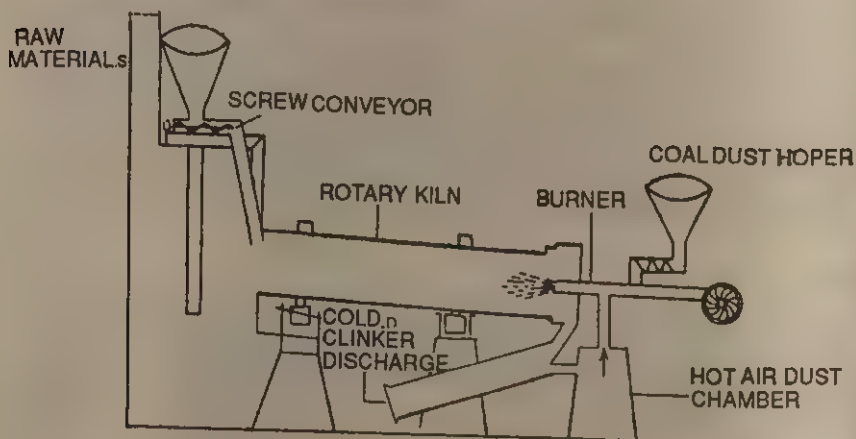
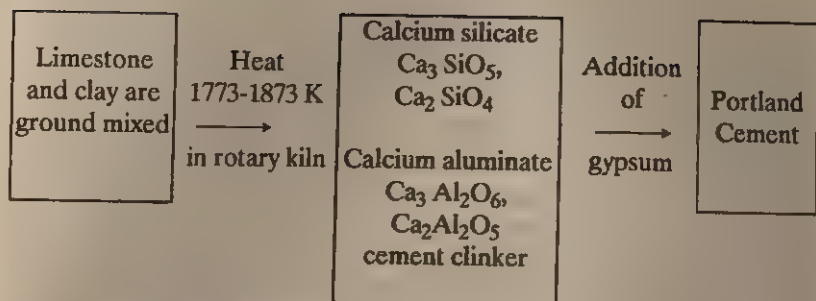


Fig. 14.14. Rotary kiln for the manufacture of cement.

The slurry (in wet process) or the dry pulverized mixture (in the dry process) is fed into the kiln with the help of a screw conveyer. The charge moves forward due to the rotary motion given to the kiln. The charge is heated by burning powdered coal, oil or gaseous fuel. The hot gases, thus, obtained are blown in from the other side with the help of a blower. The chemical reaction takes place at a temperature of about 1773K to 1873K between lime, silica and alumina producing calcium silicates, $3\text{CaO} \cdot \text{SiO}_2$; $2\text{CaO} \cdot \text{SiO}_2$ and calcium aluminates, $2\text{CaO} \cdot \text{Al}_2\text{O}_3$; $3\text{CaO} \cdot \text{Al}_2\text{O}_3$.

The resulting product which has appearance of grey coloured balls is known as clinkers. It is cooled in coolers to atmospheric temperature. It is mixed with 2-3% of its mass with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and ground to a fine powder. This product is Portland cement.



Cement, with water forms a gelatinous mass which sets to a hard solid mass. This hard mass consists of three dimensional cross links formed between-Si-O-Si-and-Si-O-Al-chains. Fly ash, a waste product from the steel industry is mixed with cement to reduce the cost. Rice husk a source of silica is used in making cement.

Uses of Portland Cement

A mixture of cement, sand and water in desired proportions is called mortar. It is used for plastering walls. When the above mixture is mixed with broken pieces of stone and some coarse sand the resulting mass is called concrete. It is used for flooring and roofing. Reinforced cement concrete (RCC) contains framework of iron bars embedded in the concrete. RCC is used for making lintels, roofs, pillars, etc.

14.13 BIOLOGICAL ROLE OF SODIUM, POTASSIUM, MAGNESIUM AND CALCIUM

Sodium potassium, magnesium and calcium are often called the metals of life. In order to appreciate their role in living organism, it would be appropriate to know about the body fluid, where these metals are found. Each cell of the human body is bathed by its own tiny pond of tissue fluid (the interstitial fluid) which provides material for its immediate needs. Transport from the environment is performed by circulatory system.

The distribution (Fig 14.15.) of the body fluid in the various compartments is as follows :

1. Cellular fluid or intracellular fluid (fluid within the cell)
2. Extracellular fluid (from outside the cell)
 - (i) Interstitial fluid (tissue fluid, the fluid present in the tissue spaces).
 - (ii) Plasma (fluid in the circulatory system.)

The intracellular fluid contains mainly K^+ and HPO_4^{2-} ions whereas the extracellular fluid contains a large amount of Na^+ and Cl^- ions and a small amount of K^+ , Mg^{2+} and Ca^{2+} ions. The plasma K^+ level is under constant watch by the human system, since this ion depresses myocardial function. An increase in plasma K^+ is extremely dangerous since it leads to cardiac arrest. Calcium present in the plasma is both in the ionic and covalent forms. About half of plasma Ca^{2+} is

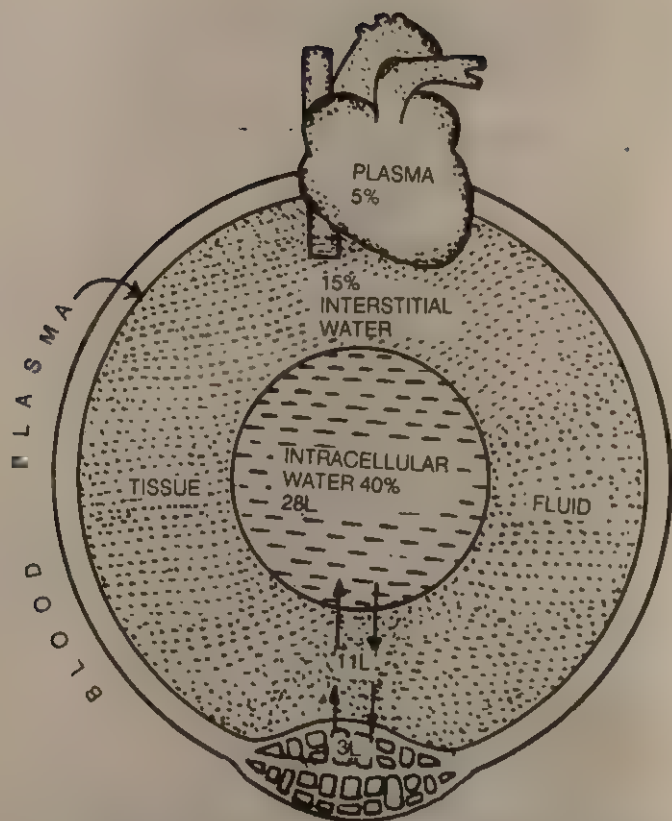


Fig. 14.15. Distribution of the total body water (fluid) in various parts, with 60% of body weight taken as an average water content.

ionic and the remainder is bound to protein. Calcium helps in the nervous system function whose deficiency causes a tetany. Plasma Mg^{2+} also shows a sedative effect on the nervous system ; with a deficit leading to hyperexcitability. The electrolyte composition of the body fluids is maintained strictly within normal limits. The cellular fluid is hardly accessible for analysis. Even tissue fluid is difficult to obtain. Under the circumstances the accessible fluid, the plasma, is used for diagnostic purposes.

In the extracellular fluid the concentration of various ions are :

$$Na^+ \text{ ion} = 142 \text{ meq/L} \quad (1 \text{ meq} = \frac{[\text{formula weight (milligram)}]}{\text{ionic charge}})$$

$$Cl^- \text{ ion} = 104 \text{ meq/L}$$

$$K^+ \text{ (Plasma)} = 5 \text{ mcg/L}$$

In order to establish this concentration gradient in the cell the membrane serves as an effective barrier, controlling the movement of these ions. Biologists propose a sodium or potassium ion transport system known as the sodium (or potassium) pump. The sodium pump ensures the necessary ratio of Na^+ and K^+ concentrations in the extracellular and intracellular spaces. Any K^+ leaking out of the cell is pumped back in; any Na^+ entering is extruded. The membrane is thus, effectively impermeable to Na^+ and K^+ . It keeps potassium within the cell, sodium out of the cell, and allows water to pass freely. The cation gradient, helps the nerve cells in discharging their functions well. A nerve cell, in the state of rest, develops potential corresponding to the potassium concentration across the membrane. When the nerve cells are in state of action, a chemical (e.g. acetyl choline) is released near its end plate, and thus the membrane potential is discharged. This discharge is transmitted through the entire length of the nerve cell by an electric pulse. This activity reflects the importance of sodium and potassium ions.

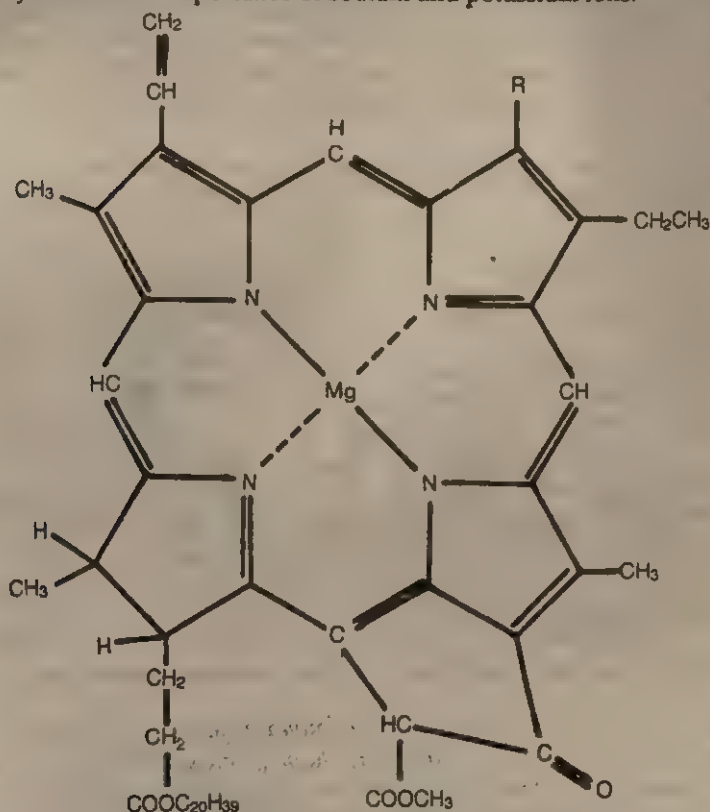


Fig. 14.16. Chlorophylls

Magnesium, an important activator for enzyme systems, shows a larger intracellular level. The high intracellular phosphate concentration is attributed to the catalyzing effect of Mg^{2+} (in conjunction with Ca^{2+}) in the phosphate polymerization step in the chain by which energy obtained from oxidation of organic compounds is stored and utilized. Magnesium is also found in chlorophylls (Fig.14.16), the pigments which are responsible for nearly all the conversion of CO_2 and H_2O to organic molecules using the energy of light (photosynthesis). Calcium is found in the bones. It has a strong bearing on the muscle contraction. More is yet known about the role of alkali and alkaline earth metals in biological functions.

Na^+ ions regulate the movement of water between cells and extracellular fluid. During dehydration plasma Na^+ level increases and water is pulled from the cell in response to the increased osmotic pressure of the extracellular fluid. (Figure 14.17) This shift continues unless water is replaced, until death occurs. Figure 14.17 shows the movement of water at the time of dehydration. Figure 14.18 shows the movement of water when the plasma Na^+ level falls, i.e. when simple dilution of the extracellular compartment with water takes place (hyponatremia).

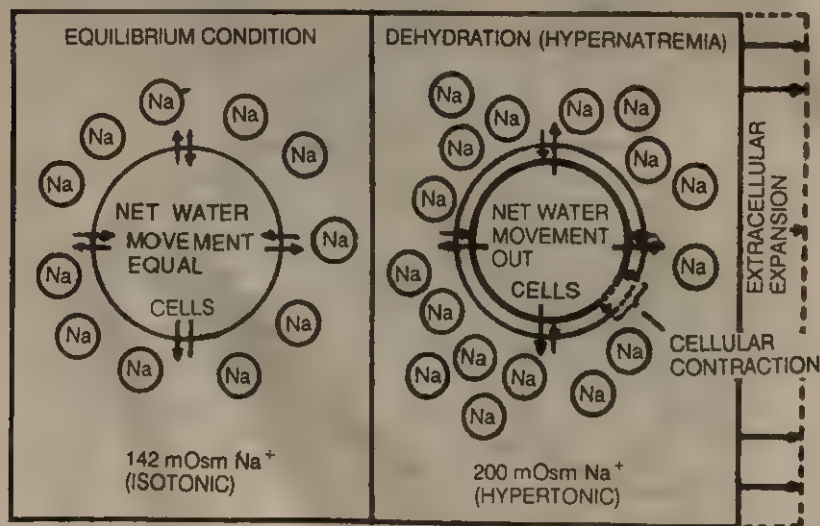


Fig. 14.17 (a) In isotonic extracellular compartment, water movement is in equilibrium. (b) Fluid shift from intracellular to extracellular fluid occurs under hypertonic conditions. The cells are dehydrated, losing water to the increasing Na^+ concentration. This will restore or expand the blood volume, depending on whether the primary condition was dehydration or hypernatremia. The cellular compartment contracts, and the extracellular

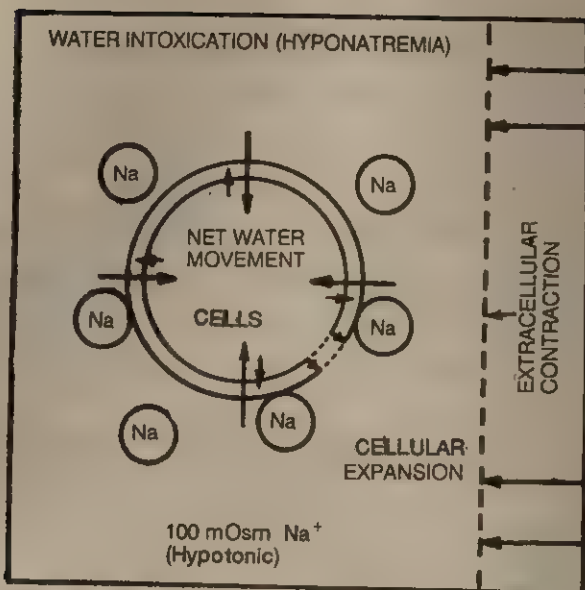


Fig. 14.18 Fluid shift from extracellular to intracellular fluid occurs under hypotonic conditions. The cellular compartment expands as water moves into saltier cells. The extracellular compartment contracts.

SELF ASSESSMENT QUESTIONS

MULTIPLE CHOICE QUESTIONS

14.1 Put a tick (✓) mark against the most appropriate choice :

- Which of the followings is not associated with the solid sodium chloride ?
(a) ionic, (b) brittle, (c) non-conductor, (d) covalent
- Which of the following alloys is an alloy of aluminium ?
(a) brass, (b) magnalium, (c) bronze (d) stainless steel
- Which one of the following properties of the alkali metals is not correct ?
(a) soft (b) low melting and boiling points (c) occur in the native state
(d) obtained by electrolysis of the molten chlorides.
- A substance used in metallurgy to remove rocky material is called
(a) slag (b) flux (c) oxidizing agent (d) gangue.
- The compound insoluble in acetic acid is (IIT 1986)
(a) CaO (b) CaCO₃ (c) CaC₂O₄ (d) Ca(OH)₂
- The pair of compounds which cannot exist together in solution is (IIT 1986)
(a) NaHCO₃ and NaOH (b) Na₂CO₃ and NaHCO₃
(c) Na₂CO₃ and NaOH (d) NaHCO₃ and Na Cl.
- A solution of sodium sulphate in water is electrolyzed using inert electrodes. The products at the cathode and anode are respectively (IIT 1987)
(a) H₂, O₂, (b) O₂, H₂ (c) O₂, Na (d) O₂, SO₂
- The metallic luster exhibited by sodium is explained by (IIT 1987)
(a) diffusion of sodium ions (b) oscillations of loose electrons
(c) excitation of free protons (d) existence of body centred cubic lattice.
- Which of the following metals is not extracted by electrolytic reduction ?
(a) aluminium (b) magnesium (c) sodium, (d) copper
- Which of the following minerals/ores is not a copper silicate ?
(a) cryolite (b) felspar (c) asbestos (d) talc
- Which of the following compounds is associated with water of crystallization ?
(a) magnesium sulphate (b) sodium hydrogen carbonate
(c) sodium chloride (d) calcium chloride.
- Which of the following ions are found in the intracellular fluid ?
(a) Na⁺ (b) K⁺ (c) Ca²⁺ (d) Mg²⁺

14.2 Fill in the blanks with appropriate words :

- (i) Sodium dissolved in liquid ammonia conducts electricity because _____ (IIT 1985)
- (ii) Dihydrogen gas is liberated by the action of aluminium with concentrated solution of _____. (IIT 1987)
- (iii) The electrical conductivity of a solution of acetic acid will be _____ if a solution of sodium hydroxide is added. (IIT 1987)
- (iv) An increase in plasma _____ level can cause cardiac arrest.
- (v) To cement clinker _____ is added to get Portland cement.
- (vi) Aluminium sulphate forms double salts called _____ with sulphates of other metals.
- (vii) In the electrolysis of purified bauxite _____ is added to lower the temperature of the melt.
- (viii) The element recovered from sea water on industrial scale is _____.
- (ix) Alkali metals are strong _____ and hence, cannot be isolated by reduction of their oxides.
- (x) Addition of water to _____ produces slaked lime.

14.3 Match the descriptions/terms in column B against the terms under Column A

COLUMN A	COLUMN B
1. Down's cell	(i) Aluminium
2. Steam	(ii) Magnesium
3. Epsom salt	(iii) Calcium
4. Flourspar	(iv) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
5. Hall's process	(v) Silicate
6. Carnallite	(vi) Sodium
7. Double salt	(vii) Alum
8. Glass	(viii) CaF_2
9. Silica	(ix) Cement
10. Anhydrite	(x) An electrolytic dissociation of molten sodium chloride.

14.4 State if the following statements are true(T) or false(F) :

1. Solubility of sodium hydroxide increases with increase in temperature (IIT 1985)
2. The softness of group 1 metals increases down the group with increasing atomic number. (IIT 1986)
3. Sodium ethoxide is prepared by reacting ethanol with aqueous sodium hydroxide. (IIT 1986)
4. Sodium when burnt in excess of dioxygen gives sodium oxide. (IIT 1987)
5. Catalyst makes a reaction more exothermic. (IIT 1987)
6. In group 1 of alkali metals, the ionization potential decreases down the group, therefore, lithium is a poor reducing agent. (IIT 1987)
7. Leaching is a process of purification and extraction.
8. Calcium sulphate is used in medicine as purgative.
9. Group 2 elements have higher m.p. and b.p. than their corresponding elements in group 1 of the periodic table.
10. The concentrated solution of sodium chloride in water is called brine.

SHORT ANSWER QUESTIONS

14.5 Write down the balanced equations for the reactions when,

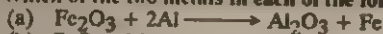
- (i) Potassium permanganate interacts with manganese dioxide in presence of potassium hydroxide. (IIT 1985)
- (ii) Calcium phosphate is heated with the mixture of sand and carbon. (IIT 1985)
- (iii) Zinc oxide is treated with excess of sodium hydroxide solution. (IIT 1986)
- (iv) Excess of carbon dioxide is passed through a solution of slaked lime. (IIT 1985)

- (v) Bauxite is treated with a hot concentrated solution of sodium hydroxide. (ITT 1986)
 (vi) Aluminium is reacted with hot and concentrated solution of sodium hydroxide.
 (vii) Sodium reacts with cold water.
 (viii) Gypsum is heated at 400K

14.6 Explain the following in one or two sentences only.

- (i) Magnesium oxide is used for the lining of steel making furnace.
 (ii) A mixture on heating with sodium hydroxide solution gives a gas which turned red litmus blue.
 (iii) Why is sodium chloride added during electrolysis of fused magnesium chloride.
 (iv) Aluminium does not react with cold water under ordinary conditions.
 (v) Calcium is used for removing traces of moisture from alcohol.
 (vi) Aluminium is placed in group 3 of the periodic table.
 (vii) In the extraction of aluminium from bauxite CaF_2 is also used.
 (viii) Sodium is not found in the earth's crust in the free form.
 (ix) Sodium is deposited at the cathode during its preparation from the brine solution.
 (x) Alloys are generally more useful.

14.7 1. Which of the two metals in each of the following reactions is more reactive ?



- (i) Which characteristic property of metals makes them more reactive ?
 (ii) Give a few properties of the aluminium which make it industrially important.
 (iii) Name the ore and the process employed for the extraction of the following metals.
 (i) Sodium (ii) Calcium (iii) Aluminium.
 (iv) Arrange the following groups of elements in order of increasing reactivity.
 (i) Na, K, Li (ii) Na, Mg, Al (iii) Na, Mg, Cu
 (v) Arrange the following metals in the increasing order of their reactivities towards water: Zn, Fe, Mg and Na.
 (vi) Suggest reasons for the following.
 (i) Caustic alkalis like sodium hydroxide are not stored in aluminium vessels.
 (ii) Aluminium cannot be extracted by reduction of its ores by carbon.
 (iii) An iron pipe, buried in the earth is protected from rusting by joining it to magnesium.
 (vii) How will you test aluminium ion in the laboratory ?

TERMINAL QUESTIONS

- 14.1** (i) Name one source in which sodium chloride is found in abundance.
 (ii) Which element is obtained if sodium hydroxide is subjected to electrolytic dissociation ?
 (iii) Name four naturally occurring substances which contain sodium. Write their chemical formulae also.
 (iv) State any three uses of sodium.
 (v) Name two elements which are placed in the same group in the periodic table.
 (vi) Name any five naturally occurring substances which contain calcium.
 (vii) Which element is obtained by the electrolytic dissociation of a mixture of calcium chloride and calcium fluoride ?
 (viii) State five uses of compounds of calcium ?
 (ix) Write the chemical formulae of calcium oxide, calcium hydroxide, calcium chloride, calcium bicarbonate.
 (x) Write the electronic arrangement in aluminium. How many neutrons does an atom of aluminium contain ?
 (xi) Why has aluminium been placed in Group 13 of the periodic table ?
 (xii) Name five naturally occurring substances which contain aluminium.

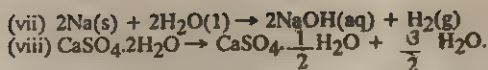
14.2

- Name three ting metals from their ores.
 (b) Name three types of compounds which are very common to many metallic ores.
 (c) Name the term assigned to the elements along with the border line between the true metals and the non-metals.
 (d) Name the various methods used in refining of the metals. Substantiate your answer by taking one example of each.

- 14.3 (a) Usual methods of extraction are not employed for the extraction of group 1 and 2 metals. Explain.
 (b) How has the problem of high temperature been solved in the electrolytic reduction?
 (c) Why is it necessary to electrolyze molten salts of sodium rather than aqueous solution of these salts in order to obtain sodium metal?
- 14.4 (a) Briefly explain each of the followings:
 (a) Down's cell (b) Leaching and (c) Aluminothermy.
- 14.5 Give in brief the extraction of aluminium from bauxite.
- 14.6 (a) Aluminium is more active than iron and yet there is less corrosion of aluminium when both are exposed to air. Explain.
 (b) A trivalent metal was obtained by the process of electrolysis. The metal, when dissolved in dilute HCl and treated with excess NH_4OH gave a white precipitate. What was the metal? How will it react with NaOH? Name one alloy of the metal.
 (c) What is activity series of metals?
- 14.7 (a) How do the metals Sodium, calcium, aluminium and magnesium. react with
 (i) water and (ii) Air
 (b) What is the action of common acids on the following metals?
 sodium, calcium, aluminium and magnesium.
- 14.8 Explain the followings:
 (a) Ionization energies of alkali metals decrease as the atomic number increases.
 (b) Group 2 metals (Mg, Ca) are harder and denser than Group 1 metals (Na, K)
 (c) It is necessary to purify the bauxite ore before electrolysis to produce aluminium.
- 14.9 How do magnesium and calcium occur in nature? Suggest the methods for their extraction?
- 14.10 What is soda ash? Discuss the method for its production?
- 14.11 Explain the significance of sodium and potassium in biological fluids.
- 14.12 Explain the followings:
 1. The hydroxides and carbonates of sodium and potassium are easily soluble in water while the corresponding salts of magnesium and calcium are sparingly soluble in water.
 2. Aluminium reacts both with acids and alkalis?
 3. Gypsum is added towards the end in the production of cement.
 4. A strip of magnesium continues to burn in sulphur dioxide.
 5. Aluminium is used for electric cables though it is less conducting in nature than copper.
- 14.13 What are alloys? Name a few alloys of magnesium and aluminium with their compositions and uses.
- 14.14 Give the methods of preparation of the following compounds. Give their uses also.
 (i) Sodium carbonate (ii) Anhydrous aluminium chloride (iii) Quick Lime and (iv) Sodium hydroxide.
- 14.15 What is cement? Give its composition and the raw materials used in its production. Describe the method briefly.

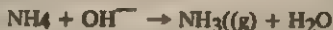
ANSWERS TO SELF ASSESSMENT QUESTIONS

- 14.1 (i) d (ii) b (iii) c (iv) b (v) c (vi) a (vii) a (viii) d (ix) d (x) a (xi) a (xii) b
- 14.2 (i) The electron is solvated (ii) sodium hydroxide (iii) increased (iv) K^+ (v) gypsum (vi) alums (vii) flourspar (viii) sodium or magnesium (ix) reducing agents (x) quicklime.
- 14.3 1. (x) 2. (vi) 3. (iv) 4. (viii) 5. (i) 6. (ii) 7. (vii) 8. (v) 9. (ix) 10. (iii)
- 14.4 (i) F (ii) T (iii) F (iv) F (v) F (vi) T (vii) T (viii) F (ix) T (x) T
- 14.5 (i) $2\text{KMnO}_4 + \text{MnO}_2 + \text{KOH} \rightarrow 3\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$
 (ii) $2\text{Ca}_3(\text{PO}_4)_2 + 6\text{SiO}_2 + 10\text{C} \rightarrow 6\text{CaSiO}_3 + 10\text{CO} + \text{P}_4$
 (iii) $\text{ZnO} + 2\text{NaOH} \rightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O}$
 (iv) $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$
 $\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Ca}(\text{HCO}_3)_2$
 (v) $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 2\text{H}_2\text{O} + 2\text{NaOH} \rightarrow 2\text{NaAlO}_2 + 3\text{H}_2\text{O}$
 (vi) $2\text{Al}(\text{s}) + 2\text{NaOH}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaAlO}_2(\text{aq}) + 3\text{H}_2\text{O}$

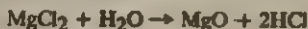


14.6 (i) MgO is used for the lining of steel making furnace as it helps in the removal of impurities of silicon, phosphorous and sulphur through slag formation. (IIT 1987)

(ii) The mixture contains NH_4^+ ion as it gives NH_3 on being heated with NaOH solution. The gas turns red litmus blue.



(iii) Because NaCl suppresses the hydrolysis of magnesium chloride and increases the conductivity of the fused mass.



(iv) Because the surface of aluminium remains covered with a thin film of oxide. If the film of oxide is removed, then aluminium reacts with water forming aluminium hydroxide and dihydrogen.

(v) Because calcium absorbs water

(vi) Aluminium has electronic configuration $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$. Accordingly, it contains three electrons in its outermost shell, hence, is placed in group 13.

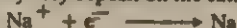
(vii) CaF_2 works as a flux. Also it is used to lower down the m.p. of purified bauxite.

(viii) Sodium is a highly reactive substance, and hence is not found in its native state.

(ix) Sodium chloride dissociates as follows :



Sodium ions, because of their positive charge, move towards cathode and are reduced there. Finally they deposit on the cathode.



(x) Because alloys are harder than metals and are corrosion resistant. They acquire attractive colour.

(4) Mg; Tendency to lose electrons. Greater the tendency of the metal to lose electrons the more reactive it is.

2. (i) light metal, (ii) good conductor of heat and electricity, (iii) strong affinity for oxygen even at ordinary temperature (iv) corrosion resistant due to Al_2O_3 layer.

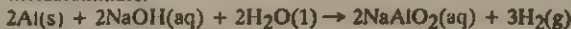
3. (i) Rock salt or NaCl from sea water. Electrolytic dissociation of molten sodium chloride or sodium hydroxide. (ii) Calcium chloride from sea water. Electrolytic dissociation of a mixture of calcium chloride and calcium fluoride.

(iii) Bauxite. Electrolytic dissociation of a mixture of alumina (from bauxite) and cryolite (purified naturally occurring substance.)

4. (i) $\text{Li} < \text{Na} < \text{K}$ (ii) $\text{Al} < \text{Mg} < \text{Na}$ (iii) $\text{Cu} < \text{Mg} < \text{Na}$

5. $\text{Fe} < \text{Zn} < \text{Mg} < \text{Na}$

6. (i) Aluminium dissolves in sodium hydroxide forming soluble sodium metaaluminate.



(ii) Aluminium is a strongly electropositive metal. Purified alumina, therefore, cannot be reduced by carbon. Moreover, aluminium, if formed, instantaneously combines with carbon to yield aluminium carbide, Al_4C_3

(iii) Magnesium is more electropositive than iron and is oxidized in preference to iron, thus, preventing the formation of Fe^{2+} and hence, rust.

(iv) **Lake test** : In an aluminium salt solution add a little litmus solution and excess of ammonium hydroxide. A blue gelatinous precipitate is formed which floats in a colourless medium (blue lake).

UNIT 15

Chemistry Of Heavier Metals

(Iron, Copper, Silver, Gold, Zinc, Mercury, Tin, and Lead)

Only through theory does knowledge, maturing into an integral whole, become scientific knowledge; science is an ordered combination of factual knowledge and theory.

A.M. BUTEROV

UNIT PREVIEW

- 15.1 Introduction
 - 15.2 Iron
 - 15.3 Steel
 - 15.4 Compounds of iron
 - 15.5 Copper, silver and gold
 - 15.6 Compounds of copper, silver and gold
 - 15.7 Photography
 - 15.8 Zinc and mercury
 - 15.9 Compounds of zinc and mercury
 - 15.10 Tin and lead
 - 15.11 Compounds of tin and lead
 - Self assessment questions
 - Terminal questions
 - Answers to self assessment questions.
-

LEARNING OBJECTIVES

At the completion of this unit, you should be able to:

1. Cite the principal sources of the heavier metals included in this unit and methods of their extraction.
2. Compare the variation in properties found among the members of the group to which the metals belong.
3. Give the composition and use of the alloys spanning the unit.
4. Give the methods of preparation, and uses of oxides, halides, sulphides and sulphates of these metals.
5. Explain the chemical principles of photography.
6. List some of the important uses of the metals and their compounds included in this unit.
7. Give the chemical formulae of the various minerals and ores covered in this unit.
8. Differentiate between the three types of iron: : Cast iron, Pig iron and Wrought iron.

9. Understand the meaning of the following terms: flux, slag, blister copper, matte, steel and steel alloy.

1																	18
2													13	14	15	16	17
		3	4	5	6	7	8	9	10	11	12						
							Fe			Cu	Zn						
										Ag			Sn				
										Au	Hg		Pb				

15.1 INTRODUCTION

From the Bronze Age to the steel age, man has used metals and particularly in the form of alloys. Copper, silver and gold have been known since the first records of history as being worked upon in the ancient civilization of Mesopotamia 4500 years ago. Some of the common metals that we encounter are tin, lead, iron, cobalt, nickel, copper, silver, gold, zinc and mercury. We usually think of metals as substances used for structural activities such as, in buildings, trains, automobiles, *etc.* Metals are used for various purposes including for fabrication purposes and to conduct heat and electricity. In addition, metals and their compounds are useful to mankind. They serve many important biological functions (Unit 14).

Modern civilization is totally dependent on the use of metals. Metals have found their use in jet aeroplane and rocket. Titanium is used in the high temperature components of jet engines and in the outer skins of supersonic fighter aircraft. Alloys are widely used for various purposes.

By now, we have gathered sufficient knowledge to distinguish between metals and non-metals (Units 12, 13 and 14). In Unit 2, we studied about the various steps involved in the extraction of metals from their natural deposits. We are already familiar with their metallic characteristics (Units 12, 13 and 14). In this unit, we shall examine the

various processes of obtaining some heavier metals, e.g., iron, copper, silver, gold, zinc, mercury, tin and lead from their ores. We are already familiar with the processes employed in the extraction of sodium, magnesium and aluminium (Unit 14). We shall also study about the chemical reactions of these metals. This unit also includes the various chemical aspects of their compounds and their uses.

15.2 IRON

Iron was known at least as early as 4000 B.C. Iron ornaments dating back to 4000 B.C. have found in Egypt. Some iron pieces have been found in the great 2900 B.C. pyramid at Giza. Iron objects have been found in archaeological excavations in the Middle East, India, China and most ancient civilization. The early discovery and use of iron in manufacturing of tools and weapons are the fruits of wide distribution of its ores and the ease with which ores could be reduced by carbon. Iron first was smelted when a fire happened to be made over a surface of ore deposit. People in ancient India knew iron making from its ores and were experts in producing steel. The iron pillar in Qutab Minar complex in Delhi is a symbol of our ancient civilization.

Iron is the most important of metals. Iron with electronic configuration $[\text{Ar}] 3d^6 4s^2$ belongs to group 8 of the periodic table. Iron is a typical transition element.

Iron is a dark grey metal. On rusting, its colour changes to brown. It is a good conductor of heat and electricity and has a high tensile strength. It is one of the few magnetic elements.

Iron has been put to various uses - from using for manufacturing various items to preparing important and useful alloys. Iron is an essential element of our bodies. It is present in the blood as an important component of haemoglobin (Fig. 15.1), an oxygen carrier in the body. Here it is present in the divalent state and is surrounded by a square planar coordinated porphyrin ring with a nitrogen base coordinated on one side of the plane and a vacant site on the other. The vacant site coordinates O_2 . Triad of iron, cobalt and nickel exhibit chemical characteristics which are more alike to each other than to the characteristics of the elements below them in the periodic table.

As expected, iron, cobalt and nickel fall in line with other elements in the first row of transition metals, e.g., in alloys and complex formation. There occurs some differences as well, e.g., Fe, Co and Ni do not form stable oxyanions like CrO_4^{2-} and MnO_4^- and variability in oxidation states.

Iron, cobalt and nickel are silvery white metals of only moderate reactivity. They are ferromagnetic in nature. They dissolve in dilute mineral acids giving respective metal ions in +2 state (Fe^{3+} in the presence of air). Both Fe and Ni are rendered passive by concentrated HNO_3 . They react with oxygen and halogens.

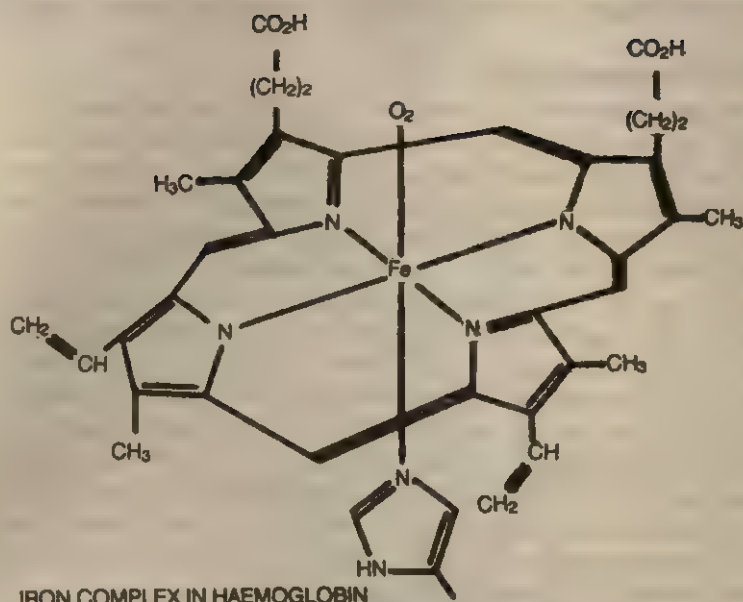


Fig. 15.1. Iron complex in haemoglobin

Some general properties of iron, cobalt and nickel are given in Table 15.1

TABLE : 15.1 General properties of iron, cobalt & nickel.

Properties	Fe	Co	Ni
Atomic number	26	27	28
Electron	[Ar] 3d ⁶ 4s ²	[Ar] 3d ⁷ 4s ²	[Ar] 3d ⁸ 4s ²
Atomic radius (pm)	126	125	125
Ionic radius(pm) M ²⁺	76	74	72
M ³⁺	64	63	62
Melting point (K)	1808	1768	1726
Boiling point (K)	3273	3173	3005
Density g cm ⁻³	7.86	8.86	8.90
Common oxidation states	+2, +3	+2, +3	+2

15.2.1 Occurrence and Extraction

Iron does not occur native in the earth's crust. However, it is abundantly found in the combined form, mainly as oxides and sulphides. The common and important ores are : (i) haematite, Fe₂O₃, (ii) magnetite, Fe₃O₄, (iii) iron pyrites, FeS₂ (iv) limonite or brown iron ore, Fe₂O₃·H₂O, and (v) siderite, FeCO₃. It makes 5% of the earth's crust.

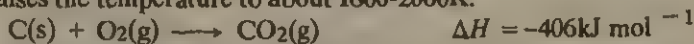
In India, iron deposits are mainly found in Bihar, West Bengal,

Orissa and Karnataka. Asansol, Durgapur, Jamshedpur, Bhilai, Bokaro, Rourkela and Bhadravati are the main iron producing centres from its ores.

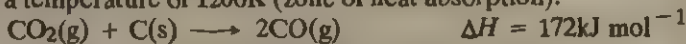
Isolation of Iron from its Ores

The most important raw materials from which iron is obtained are haematite and limonite. Other minerals containing iron, such as sulphides must be roasted in air to get the oxide before reduction to the metal. And carbonates are heated in the absence of air (calcination) to obtain oxide. In these processes, the volatile impurities are removed and the ore becomes porous. In the earth, iron ores are found mixed with clay, silica and compounds of various elements including manganese, phosphorus and sulphur. Purified iron oxide is reduced by carbon monoxide in a blast furnace. A blast furnace is a tall steel structure lined with fire bricks (Fig.15.2). The roasted ore mixed with limestone and coke is fed into the blast furnace from the top and a blast of hot air is introduced at the bottom. The coke serves as a source material for CO, the reducing agent. Limestone serves as a flux material. The following reactions take place:

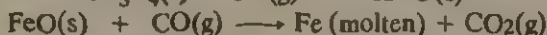
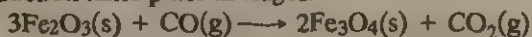
(i) In the lowest part (zone of combustion) of the furnace coke is oxidized exothermically to carbon dioxide. The highly exothermic reaction raises the temperature to about 1800-2000K.



(ii) As the hot carbon dioxide rises, it reacts with heated coke to form carbon monoxide. This reaction is endothermic. The furnace in this region has a temperature of 1200K (zone of heat absorption).

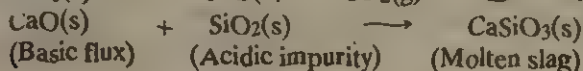


(iii) In the region (700-1000K) just above the zone of heat absorption, iron oxide is reduced exothermically by the upward moving CO. The reduction takes place in stages.



The iron produced finds its way to the bottom of the furnace where the temperature is high enough to melt it. The molten iron gets accumulated at the bottom of the furnace.

In the meantime, the limestone is decomposed by the intense heat of calcium oxide (a basic anhydride) and carbon dioxide. The calcium oxide reacts with silica (the main impurity in the ore) forming a low melting calcium silicate (slag) which collects as molten slag above the layer of molten iron at the bottom of the furnace. Molten slag protects iron from oxidation.



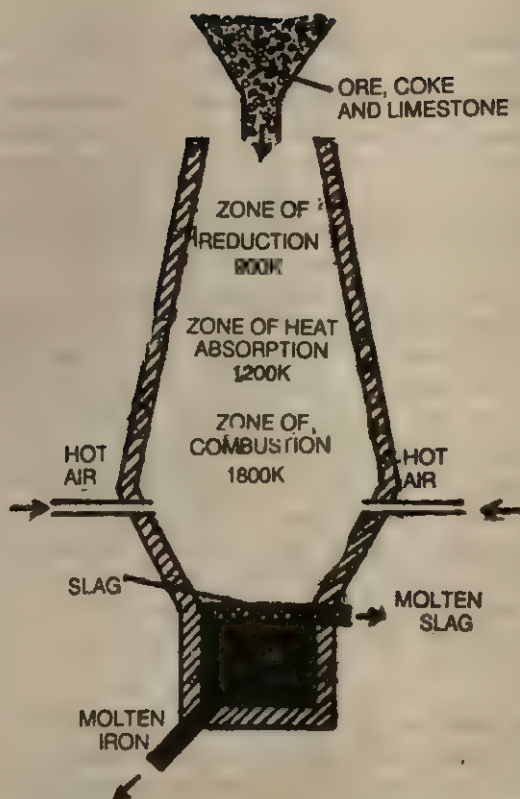


Fig. 15.2. The smelting of iron oxide in the blast furnace.

In the uppermost region, temperature decreases to about 500K where the raw materials are added.

Slag and iron are tapped off every few hours and collected separately through different outlets. The iron from the lower outlet of blast furnace is run regularly into sand moulds where it forms solid blocks called 'pigs'.

15.2.2 Forms of Iron

Different forms of iron have been recognised depending upon the content of carbon. There are three commercial forms of iron: Pig iron, or Cast iron, Steel and Wrought iron.

Pig Iron: It is a primary product of the blast furnace, contains considerable amount of impurity in the form of silicon, carbon (3-5%), phosphorus, sulphur and manganese. These can be removed by passing limited supply of air through the molten metal. Pig iron is very hard and brittle due to its high carbon content. It is classified according to its

composition and the type of steel making process for which it is destined.

Cast Iron: It is the moulded form of pig iron. It is obtained by pouring pig iron directly from the blast furnace into moulds of desired shapes. It is very hard and brittle because of its high carbon content (carbon is present either as graphite or as iron carbide, cementite - Fe_3C). **White Cast iron** contains cementite. It is produced by cooling the molten iron (from blast furnace) quickly. Cast iron (m.p. 1475K) containing carbon in the form of graphite is called **grey cast iron**. It is obtained by cooling the molten iron slowly. Its tensile strength is low. It is easy to melt. It cannot bear any mechanical or thermal shock, hence, it is unfit for structural uses. It cannot be forged or welded by hammering. When molten cast iron solidifies, it expands slightly. Because of this property, it is extensively used in casting various shaped articles, e.g., toys, stools, tubes, tools and agricultural implements. It is highly resistant to corrosion and is used for moulding sewage pipes and similar such things. It is used in engine blocks, brake drums, transmission housing in automobiles, gutter piping, railings, etc. It is also used to manufacture bed plates of various machines and lathes, lamp posts, hot-water pipes, grids, man-hole covers, fly wheels, slabs, tubes, bunsen burners, railings, etc.

Wrought Iron: Iron containing carbon from 0.2 - 2% is called steel. Iron having carbon below 0.2% is called wrought iron (also called malleable iron). It is the purest form of commercial iron (iron 99.5%, 0.5% other impurities including carbon). It is prepared by oxidizing the impurities present in pig or cast iron in a reverberatory furnace coated with haematite. Oxidized sulphur, silicon and phosphorus are removed as slag.



The product is then passed through rollers to remove slag. As a result, some of the slag is left between the layers of iron. Thus, it assumes a fibrous structure. Wrought iron (m.p. 1675K) is tough, malleable, ductile and can be welded at 1275K. The presence of slag in iron makes it tough and resistant towards rusting and corrosion. It can be hammered, forged, rolled, drawn and pressed into various shapes. Its melting point is higher than that of cast iron. It is used for making various types of articles, chains, anchors, nails, bolts, frame-works, wires, electromagnets for electric cranes and dynamos, horse-shoes, agricultural implements, railway carriages couplings, etc. It is also used for some ornamental works.

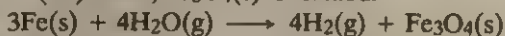
15.2.3 Reactions of Iron

(i) **Action of air** : Iron does not combine with dioxygen at ordinary temperatures, but when strongly heated it burns to form Fe_3O_4 which is magnetic in nature.



Iron, in the presence of moist air, gets covered with a brownish red layer known as rust. Rust is a mixture of hydrated oxides of iron ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$)

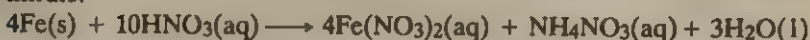
(ii) **Action of water**: Iron reacts with water and air to form rust. When steam is passed over red hot iron, dihydrogen is liberated and iron (II) iron (III) oxide, $\text{Fe}_3\text{O}_4\text{(s)}$ is formed.



(iii) **Action with acids**: With dilute hydrochloric and sulphuric acids, an iron (II) salt and dihydrogen are formed.



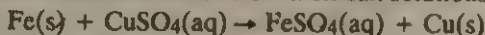
With dilute nitric acid, it gives ferrous nitrate and ammonium nitrate.



Some other products, including oxides of nitrogen, are also produced depending on the concentration and temperature. Concentrated nitric acid makes iron 'passive' *i.e.*, there is no apparent reaction. With hot concentrated sulphuric acid, it gives sulphur dioxide and a mixture of iron (II) and iron (III) sulphates.

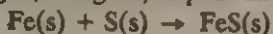


(iv) **Reaction with salt solutions** : Iron displaces metals lower in the electrochemical series from their salt solutions.



(v) **Reaction with alkalis**: Alkalis have no action on iron.

(vi) **Reaction with non-metals**: Iron combines on heating with nitrogen, halogens, sulphur and carbon.



15.3. STEEL

Iron by itself is not very useful, but the addition of metals and carbon converts it to steel. Thus, steel is an alloy of iron and carbon. Steel is not a single alloy of iron. It includes hundreds of different alloys that have carbon content ranging from 0.2% to 2% and the other added metals such as nickel, chromium and vanadium, *etc.* Steel may be broadly classified on the basis of carbon content.

Low carbon steel	:	less than 0.2% of C
Mild steel	:	0.2 to 0.3% of C

Medium carbon steel	:	0.3 to 0.6% of C
High carbon steel	:	more than 0.6% of C.

To produce steel from pig iron, the impurities like silicon, phosphorus and sulphur are converted to their oxides. Later, desired amount of manganese and other materials which are needed to impart the desired characteristics to the steel, are added. Gaseous oxides remove themselves; other oxides are removed by combination with a base such as calcium oxide to form a slag.

As usual hardness of steel also depends upon carbon content and heat treatment. On heating further to 1123K and then on sudden cooling it by plunging into cold water, it becomes harder and brittle. This treatment is called 'quenching'. By reheating the quenched steel to carefully regulated temperature, *i.e.*, between 503K to 573K and then cooling, brittleness disappears and hardness is retained. This process is known as 'tempering'. The heating of the steel to a temperature well below red heat followed by slow cooling is called 'annealing'. The steel so produced is quite soft. The processes employed for the manufacture of steel are :

1. The Bessemer process
2. The open hearth process
3. The basic oxygen process
4. The electric arc process.

1. The Bessemer Process : Pig iron is treated in the Bessemer converter (Fig. 15.3). It is a pear shaped steel vessel with a refractory lining. The refractory of lining may be either of silica (acidic Bessemer) or a calcined dolomite (basic Bessemer - removes phosphorus and silica as calcium and magnesium silicates and phosphates) depending upon the nature of impurities to be removed from the molten iron. The converter is charged with molten iron from the blast furnace, and a blast of preheated air is blown into the molten iron through a series of holes (tuyeres) provided in the bottom. The initial temperature rises to 873K. As a result, impurities are oxidized. These oxidized impurities are slagged off by lining and start floating on the surface of the molten metal (basic slag is used as a phosphate fertilizer).

Most of the carbon is converted to carbon monoxide which burns in air with a blue flame (disappearance of blue flame indicates the completion of the operation). When the entire oxidation process is over, a calculated amount of carbon and alloying elements are added. The molten steel is poured into moulds or ladles.

Generally, an acidic Bessemer converter is employed (also when amounts of phosphorus and silica are small). It is the usual practice to add some scrap iron to the converter followed by molten pig iron. The oxidation reaction is highly exothermic which involves a variety of reactions. Some of the typical reactions are given in Section 2.6.4 (Unit 2).

2. The Open Hearth Process: This process was developed by William Siemens and Martin (1960). The furnace (Fig. 15.4) used for the

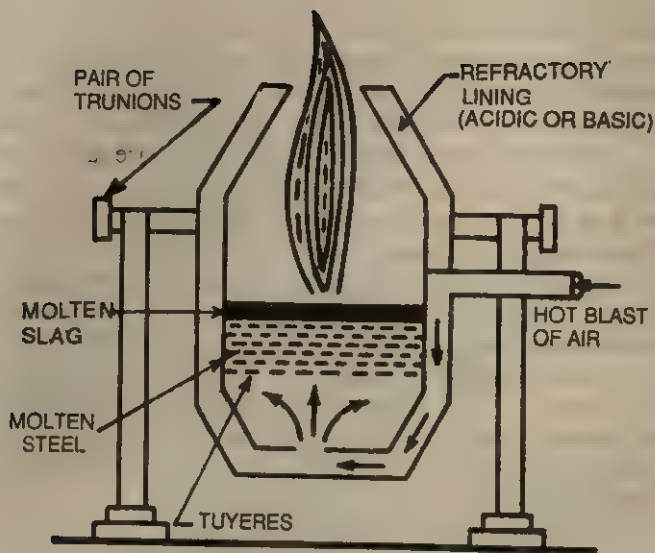


Fig. 15.3. A Bessemer converter for producing steel

purpose works on a regenerative principle. The fire brick lining of the furnace can be either acidic (SiO_2) or basic (calcined dolomite) depending upon the nature of impurities. Pig iron (or cast iron) along with scrap iron, concentrated haematite and limestone is fused. The furnace is heated to about 1973K by producer gas or a mixture of gases (natural gas) and air (over the metal). The direction of gas and air flow are reversed

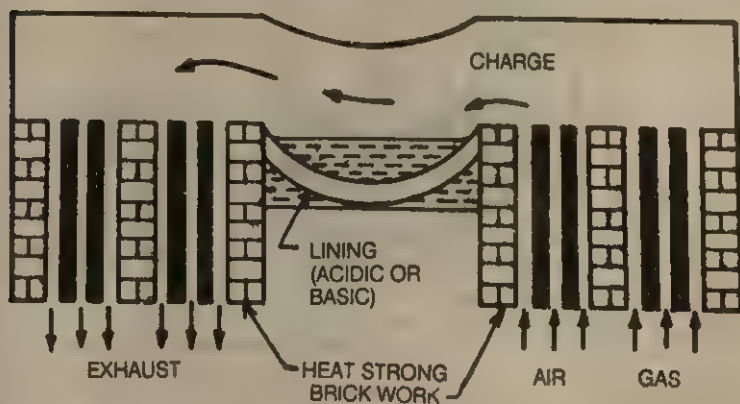


Fig. 15.4. The open hearth process for producing steel.

periodically. This conserves much of the heat energy of the oxidation process and keeps the iron in the molten state for long periods of time. The oxidation reactions are quite similar to those taking place in the Bessemer converter. Conversion of iron into steel is done at Bhilai by this process. A steel of more exact composition is obtained by this method.

3. The Basic Oxygen Process : This process is much in use these days and is an improvement over the Bessemer process. The compressed (~ 10 atm) oxygen gas and a stream of powdered limestone are fed through a water cooled lance and discharged above the molten metal (Fig. 15.5). The purified iron being denser than the impure one, gets accumulated at the bottom. The process is rapid, and hence, economical. It requires scrap iron only in very small amounts. Most of the steel is produced by this method. This process is popularly known as LD process or Litz-Donawitz process (Litz and Donawitz are two towns in Austria where this process was employed for making steel.) This method is employed at Rourkela for conversion of iron to steel.

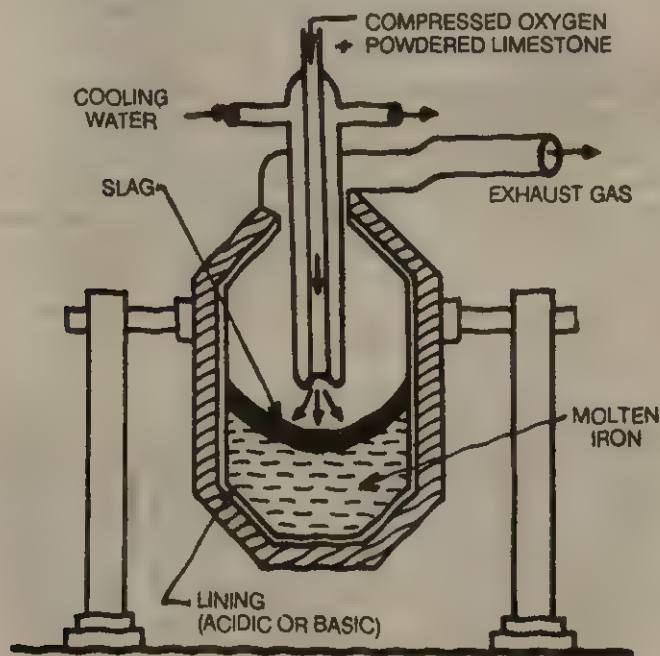


Fig. 15.5 The basic oxygen process for manufacturing steel

4. The Electric Arc Process: Today, a considerable amount of steel is produced by this process. It gives a high quality steel and of exact composition. It is not necessary to use molten iron in this process. The

layout of the furnace is given in Fig. 15.6. Steel scrap is charged into the furnace and a powerful electric current is passed through the electrodes. The heat generated from the electric arc melts the metal. Limestone and iron oxides are added at this stage which combine with the impurities forming slag. Slag is tapped off the metal and molten steel is poured into teeming ladle and finally transferred into moulds.

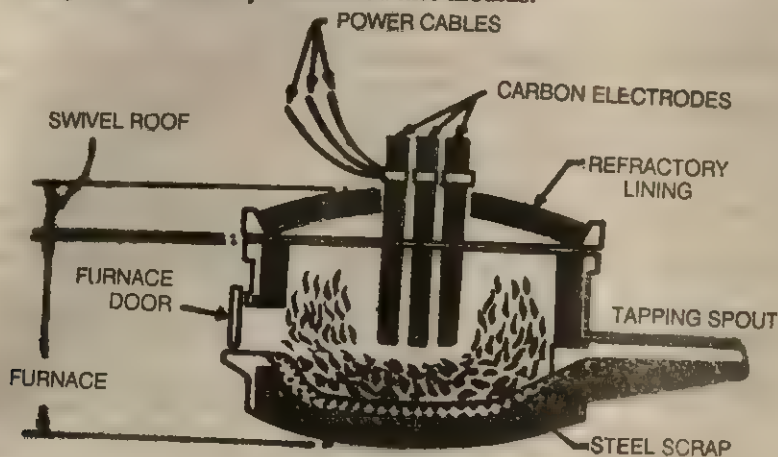


Fig. 15.6. The electric arc furnace.

15.3.1 Alloy Steels

Alloy steels are alloys of carbon, small percentages of usual impurities associated with iron and the desired amounts of other metals, such as, nickel, cobalt, manganese, chromium, vanadium, *etc.* Pure iron is not good for most of the purposes. Added metals produce great differences in the properties of iron. Thousands of alloys are known. Stainless steel is the most important example of alloy steel. As the name goes, it is not stained or corroded by air, water, dilute mineral acids or alkalis. Eighteen-eight stainless steel is one of the many stainless steels and is very common. It contains 18% chromium, 8% nickel and rest steel. India has got vast sources of manganese and not of nickel. Stainless steel containing manganese has been produced here. It finds its wide use in making household ware, watch cases, shaving blades, *etc.* Some of the alloy steels with their compositions, typical uses and properties are given in Table 15.2.

15.4 COMPOUNDS OF IRON

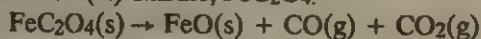
Iron forms two series of simple compounds, *i.e.*, ferrous and ferric with +2 and +3 states respectively. Iron forms complex compounds and double salts. Mohr's salt, a double salt of ferrous sulphate and ammonium sulphate will be discussed here alongwith some other useful and important compounds, *e.g.*, oxides, halides, sulphides and sulphates.

TABLE 15.2. Some alloy steels

Alloy steel	Composition	Chief properties	Uses.
1. Nickel steel	Ni 3.5%	Hard, corrosion resistant, flexible	For cables, safes, rails, armour plates, heavy machinery, propeller shafts, etc.
2. Molybdenum steel	Mo 1-3%	Hard, heat resistant	For axles, autos, cutting tools
3. High speed steel	W 18%, Cr 4%, Mn 0.3%	Very hard, retains temper at very high temperatures	For drill bits, cutting tools
4. Chrome steel	Cr 1.5-2%	Hard, resistant to corrosion	For armour plates, heavy crushing machinery, cutlery
5. Tungsten steel	W 14-20%, Cr 3-8%	Hard even at red heat, strong	For high speed tools, drill bits
6. Chromium vanadium steel	V 0.15%, Cr 1%	Good tensile strength and load bearing	For springs, shafts axles, frames, cog-wheels etc.
7. Manganese steel	Mn 12-15%	Very hard, resistant to corrosion, high melting.	For rails, safes, armour plates, heavy machinery, jaws of rock crusher.
8. Invar	Ni 36%	Extremely low expansion on heating	For clock pendulum, measuring tapes.
9. Alnico	Al 12%, Ni 20%, Co 5%	Highly magnetic	For making permanent magnets
10. Stainless steel	Cr 11.55%	Corrosion resistant	For cycle and automobile parts.

15.4.1 Oxides Of Iron

Iron forms three oxides: FeO , Fe_2O_3 and Fe_3O_4 . We are already familiar with these oxides. Iron (II) oxide (FeO) is obtained by thermal decomposition of iron (II) oxalate, FeC_2O_4 .



The oxide is basic in nature and can be used for preparing iron (II) salts on treating with acids.

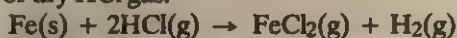
Iron (III) oxide, (Fe_3O_4) occurs in nature as the universal haematite. It can be obtained by igniting $\text{Fe}(\text{OH})_3$ or by roasting iron pyrites, FeS_2 in the air. It is amphoteric in nature and forms (III) salts with acids and ferrates (III) like NaFeO_2 , with alkali. It is red in colour and is used as a paint pigment, under the names 'rouge' and 'venetian red'.

Iron (II,III) oxide (Fe_3O_4) is a mixed oxide, FeO , Fe_2O_3 , called magnetic oxide of iron or loadstone. It occurs extensively in nature as the ore, magnetite

15.4.2 Halides Of Iron

Both $\text{Fe}(\text{II}) \text{Cl}_2$ and $\text{Fe}(\text{III}) \text{Cl}_3$ are known. 'Pale green' crystals of iron (II) chloride $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ is produced by the action of dilute HCl ,

followed by crystallization. The anhydrous salt is prepared by heating iron in a stream of dry HCl gas.



It can be easily oxidized to FeCl_3 by passing Cl_2 gas through its solution in water.



Ferric Chloride, FeCl_3 : Anhydrous ferric chloride is prepared by heating iron in a stream of dry chlorine gas (Fig. 15.7).

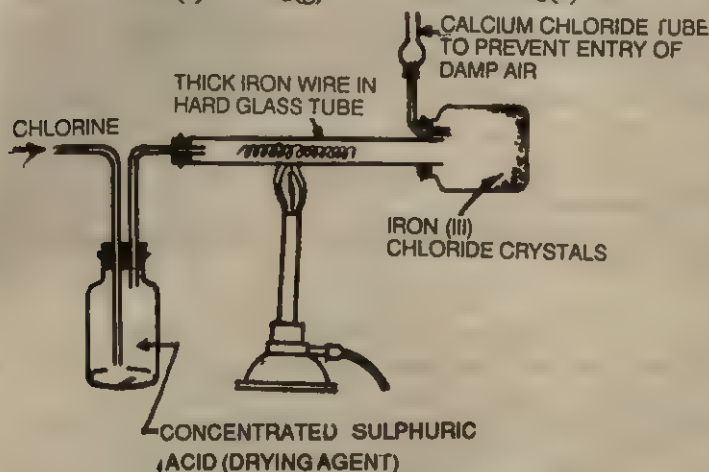
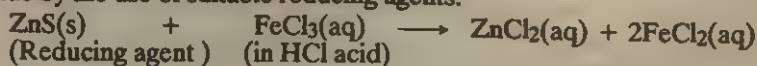


Fig. 15.7 Preparation of iron (III) chloride.

It readily vapourizes, and condenses in the form of dark red crystals. The aqueous solution of the salt is obtained by treating ferric hydroxide with dilute hydrochloric acid. On evaporation yellow crystals of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ separate.

Anhydrous sample of FeCl_3 cannot be prepared from the aqueous salt as it is easily hydrolyzed. It is a deliquescent solid (m.p. 575K and sublimes). It is soluble in water, alcohol, water and ether. Ferric chloride dimerizes in the vapour state (Fig. 15.8). The aqueous solution shows acidic behaviour to litmus. In strongly acidic solution, the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is colourless. Aqueous solutions of Fe^{3+} are yellow to brown in colour. This colour change is attributed to the presence of $(\text{FeOH})^{2+}$ and $[\text{Fe}(\text{OH})_2]^+$. Ferric chloride forms double salts, e.g., $\text{KCl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$ and $\text{NH}_4\text{Cl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$. Ferric chloride can be reduced to iron (II) chloride by the use of suitable reducing agents.



Ferric chloride is used as a laboratory reagent. It is effectively used in medicines as an astringent and as an antiseptic in the form of tincture,

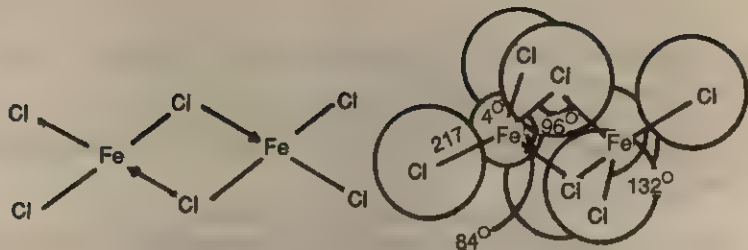
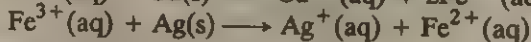
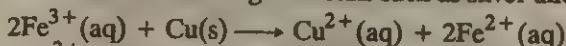


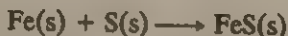
Fig. 15.8. Dimer of FeCl_3 . It decomposes above 973K .

aqueous solution and iron glycerine. It is also employed as mordant in dyeing because it furnishes $\text{Fe}(\text{OH})_3$ (essential mordant) on hydrolysis. Its oxidizing action has been quite helpful in block making. Concentrated solution of FeCl_3 is used in etching on metals such as silver and copper.

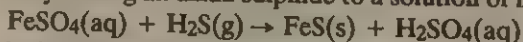


15.4.3 Sulphides of Iron

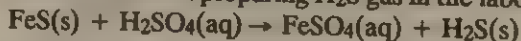
Iron (II) sulphide is usually prepared by the direct combination of iron and sulphur.



It can also be obtained by passing H_2S gas through a solution of an iron (II) salt or by adding an alkali sulphide to a solution of iron (II) salt.



It is a black solid used in preparing H_2S gas in the laboratory.

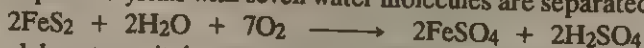


15.4.4 Sulphates of Iron

Both iron (II) and iron (III) sulphates are known.

Ferrous Sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$: It is the most important salt of iron. Commercially it is known as green vitriol because of its green colour. It occurs in nature as copperas (seems to be formed by weathering reactions from iron pyrites).

This industrially and medicinally important compound is usually manufactured by weathering actions (action of air and water) on iron pyrites at ordinary temperatures. The solution is treated with scrap iron to free from sulphuric acid and to reduce ferric sulphate formed during the course of slow reactions. On slow concentration or evaporation, ferrous sulphate crystals with seven water molecules are separated.



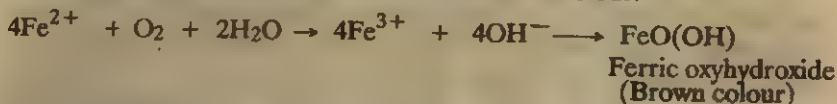
In laboratory, it is prepared directly either from iron filings or Kipp's waste. Iron filings on reacting with dilute sulphuric acid give light pale green solution from which the crystals of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ can be obtained. Kipp's waste, a solution of mainly ferrous sulphate with

unreacted sulphuric acid, is heated in the presence of scrap iron. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ crystallizes out on concentrating and allowing the solution to stand.

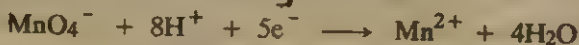
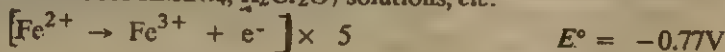
Green monoclinic crystalline $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (m.p. 338K) is isomorphous with the heptahydrates of the other transition metal sulphates and Epsom's salt, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. It loses water of crystallization in stages and finally a white anhydrous salt is obtained. On strong heating it decomposes to oxide.



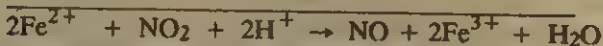
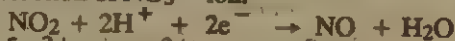
On exposure to air it loses a part of water of crystallization (efflorescence) and outer surface assumes brown colour.



It is an effective reducing agent since it gets oxidized readily to Fe^{3+} . It reduces KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ solutions, etc.



Similarly, nitrogen dioxide, NO_2 is reduced. The reduction product, NO forms a black coloured compound, $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$. The formation of this compound is the basis of **brown ring test** employed for the detection of NO_3^- ion.



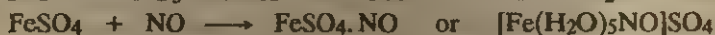
Ferrous sulphate forms double salts with ammonium and alkali metal sulphates, e.g., $\text{M}_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{K}^+, \text{Rb}^+, \text{Cs}^+$ and NH_4^+). Double salt with $(\text{NH}_4)_2\text{SO}_4$ is called Mohr's salt.

Ferrous sulphate is used for the manufacture of blue-black ink, as mordant (as it provides $\text{Fe}(\text{OH})_2$ on hydrolysis), as insecticide in agriculture and in dyeing and tanning industries. Its double salt, Mohr's salt, is used as a standard solution in the volumetric estimation of some oxidizing agents. Anhydrous ferrous sulphate is used in medicines to fulfil the deficiency of iron in food. It is employed as reducing agent in industries.

Brown ring test

To a cold solution of NO_3^- ion, freshly prepared ferrous sulphate solution is added and then followed by concentrated H_2SO_4 along the walls of test tube. H_2SO_4 forms the lower layer (denser than aqueous solution of FeSO_4). On the junction of two layers a brown ring appears. Some heat is produced which is sufficient to initiate the reduction of

NO_3^- ion to NO (forms a brown complex with FeSO_4). On stirring the solution, the ring disappears as a result of heat produced during mixing of H_2SO_4 with aqueous solution and the whole solution becomes black. The following reactions take place:



The brown colour, which appears to be due to charge transfer, evidently arises from a cationic iron nitrosyl complex; it is therefore formulated as $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ in which iron is in +1 oxidation state.

Ferrous ammonium sulphate, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$: It is prepared by mixing the solutions in equimolecular proportions of each $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_4$. On concentrating the solution the bluish-green monoclinic crystals of double salt separate.

This salt does not effloresce in air. It is quite stable and is not readily oxidized in open air. In solution, it gives test for all its constituents (Fe^{2+} , NH_4^+ and SO_4^{2-} ions). The crystals of salt are different from the crystals of both $(\text{NH}_4)_2\text{SO}_4$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

Its reasonable stability has made it useful for the volumetric estimations. Its standard solution can be prepared directly.

Iron (III) ammonium sulphate $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, known as ferric alum, is industrially important.

15.5 COPPER, SILVER AND GOLD

The coinage metals copper (Cu), silver (Ag) and gold (Au) belong to group 11 of the periodic table. They have $(n-1)d^{10}ns^1$ outer electron configuration and may be classified as transition elements in that they have valence electrons in two shells. Each has one electron in its outermost shell and eighteen in the penultimate shell. Because both the alkali metals and the coinage metals have one electron in their outermost shell, the members of these two families might be expected to behave similarly. The elements of both the groups are good conductors of electricity and form a large number of univalent compounds with similar formulae (Na_2O , Ag_2O ; NaCl , AgCl ; Na_2SO_4 , Ag_2SO_4), but beyond this, similarities between the two groups are hardly seen.

This is a group of weak electropositive metals. Gold is highly inactive, and inert resembling the platinum metals in many respects. Copper, silver and gold can use one or two electrons from the underlying shell in bond formation. Thus, Cu, Ag and Au each exhibit +1, +2 and +3 oxidation states. The most common oxidation state for copper is +2, for silver +1 and for gold +3. Silver and gold exhibit a few similarities with copper and, in fact, do not bear a great resemblance to each other. Common chemical features are seen in +1 and +3 states. Some physical properties of the group 11 metals are given in Table 15.3.

These elements have been known to mankind since ancient times. Copper was used by the Sumerians as early as 3000 BC for making tools.

Copper mixed with tin produced bronze, the first synthetic alloy, which was culturally so important to the development of ancient civilization that

TABLE : 15.3 Physical properties of the coinage metals

Properties	Cu	Ag	Au
Atomic number	29	47	79
Atomic radius (pm)	117	135	134
Ionic radius; M^{+} (pm)	93	121	137
Density ($g\ cm^{-3}$)	8.9	10.5	19.3
Ionization potential ($kJ\ mol^{-1}$) 1st	745	731	889
2nd	1959	2123	1939
3rd	3551	3830	2943
Melting point(K)	1356	1234	1336
Boiling point(K)	2868	2483	3243
Stable oxidation states	+1, +2	+1	+3
Abundance in earth's crust (ppm)	70	0.1	0.005

archaeologists have designated a period of prehistory as the 'Bronze Age'.

Because of their traditional use for coins, earlier they were called coinage metals. They have become too valuable to be used extensively in modern coins. Except for special commemorative coins, gold and silver coins are no longer in current use. Silver is now used primarily in photography and for jewellery purposes. Copper is mainly used for transporting electricity and for some other purposes where its inertness is required.

Gold, the most glamorous metal of all, is an excellent conductor of electricity and thus finds use as electrical contacts in miniature circuits. Gold is, in most people's mind, the only metal with true inherent value.

15.5.1 OCCURRENCE AND EXTRACTION

Copper

Copper, in limited quantities, is found 'native' in a few places. The chief ores are copper pyrites, $CuFeS_2$ and copper glance, Cu_2S (or CuS).

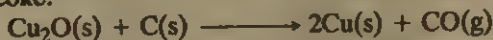
Other natural sources of copper cuprite, Cu_2O ; metaconite, CuO ; green malachite, $CuCO_3.Cu(OH)_2$; and blue azurite, $2CuCO_3.Cu(OH)_2$.

Copper is found in traces in plants found in the regions where there are copper ores. Brightly coloured feathers of certain birds have copper in trace amounts. It is also found in the blood of certain marine animals such as lobsters, oysters and cuttle fish, where it functions as oxygen - carrier.

Copper deposits are found in India at Singbhum (Bihar), Khetri (Rajasthan) and Karnataka. It is also found at various places along the outer Himalayas - Kuch, Garhwal and Sikkim, Malachite and Cuprite ores are found in Mosaboni area.

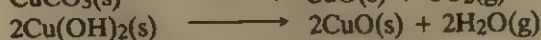
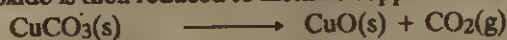
Extraction of copper from its ores depends upon the nature of the ore.

To extract copper from purified cuprite, the ore is strongly heated with coke.

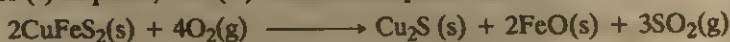


Carbonates decompose on strong heating to give copper oxide.

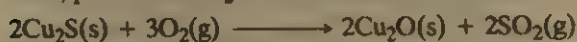
The oxide is then reduced to metallic copper on heating with coke.



In the extraction of copper from copper pyrites, the ore is crushed and concentrated by froth flotation. The ore is then roasted in air to form copper (I) sulphide, iron (II) oxide and sulphur dioxide.



Also, part of the Cu_2S is converted to the oxide.



The roasted ore is then heated with sand and coke in a blast furnace (Fig. 15.9). Iron (II) oxide combines with sand to form molten slag which floats on the molten copper (I) sulphide and can be collected separately.

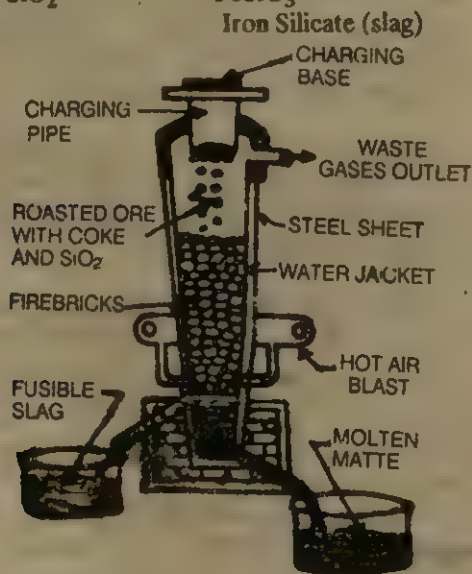
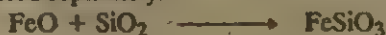


Fig.15.9 Blast furnace for the reduction of roasted copper ore.

Unreacted molten Cu_2S , alongwith other metallic sulphides forms a mixture called matte. The matte is transferred from the blast furnace to a

Bessemer converter coated inside with SiO_2 (Fig. 15.10). Compressed air alongwith sand is blown through the matte until the whole of sulphur is converted to sulphur dioxide. When iron is completely slagged off, cuprous sulphide reacts with cuprous oxide to form copper. This process is known as **Bessemerization**.

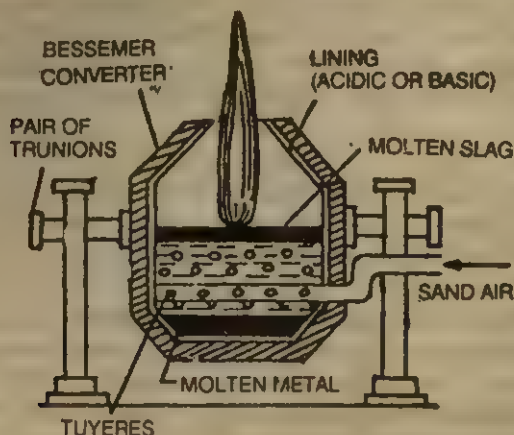


Fig. 15.10. Bessemerization of copper

The molten mass is transferred into sand moulds where it gets solidified. It contains 98% copper and is popularly known as **blister copper** because it releases bubbles of SO_2 as it solidifies, and, therefore, gets a rather blistered appearance. Impure blister copper is further purified electrolytically (Unit 2)

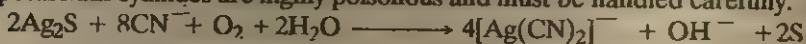
SILVER

Silver is sometimes found in large nuggets. Its chief ore are argentite (silver glance), Ag_2S ; horn silver, AgCl ; and pyrargyrite (ruby silver) $\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$. The silver content in these ores is small (about 1%). It is often found alloyed with gold, copper or mercury. Its sulphides ore usually occurs alongwith the sulphides of lead, copper, nickel, arsenic and antimony.

Most of the silver produced comes as a byproduct of the extraction of base metals, chiefly lead and copper, but also zinc, nickel and tin. Silver is also produced to a small extent from the gold ores in the Kolar gold fields in Karnataka and in the Anantpur mines. India does not have silver ores.

Powdered ores of silver are treated with dilute sodium cyanide solution (0.5%) for several hours in the presence of air. A soluble and

stable complex of silver with cyanide ions is obtained. Sodium and potassium cyanides are highly poisonous and must be handled carefully.



The silver is precipitated from the soluble cyanide complex by adding zinc metal or aluminium.



Plenty of silver is obtained from the anode mud formed during the electrolytic refining of copper (Unit 2). Silver can be obtained from ores containing free silver chloride by amalgamation process. Powdered ore is mixed thoroughly with mercury. Mercury dissolves the free silver and reduces the silver chloride to the metal, which also dissolves in excess of mercury.



The amalgam is separated and distilled in iron retorts. The mercury vapours are condensed and used again, whereas the silver remains in the retort. Electrolysis of silver nitrate solution gives pure silver.

GOLD

Gold is found mainly as the metal, occasionally in nuggets scattered through gravel but more frequently as small particles in veins of quartz or alluvial sands of rivers that pass over auriferous rocks. Native gold always contains silver and some platinum metals (Ru, Rh, Pd, Os, Ir and Pt). It is found associated with sulphides of iron, copper, lead, antimony and arsenic. It has also been found alloyed with silver. In the combined state, gold is found in a few minerals such as the telluride, AuTe_2 , sulphide and arsenosulphide. A major share of gold production all over the world is from the mines in South Africa. USSR, USA, Canada and Australia also occupy the position amongst the gold producing countries. India occupies the eighth position. Its contribution is about 2% of the world production. Our major (~ 99.97 %) production is from the Kolar mines in Karnataka. Alluvial gold is found scattered in Chhota Nagpur. Gold washing is mostly done in Singhbhum and Manubhum (Bihar) in the valleys of the Suvernareka river.

Native gold is separated from the dirt by washing with water and then dissolving in liquid mercury with subsequent distillation. Mercury distills over leaving behind the gold. Now-a-days powerful streams of water are thrown against the deposits, which are washed into the sluices (long troughs). This process is called hydraulic mining.

The cyanide process for gold is similar to that used for obtaining silver from the ores; in fact two metals are usually extracted together. Gold ore is first concentrated by froth flotation process and then roasted to remove all the oxidisable impurities, e.g., Te, As, and S. The roasted ore is ground to a fine slime in sodium cyanide solution and aerated by agitation for two days.



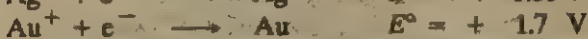
Gold is recovered from the solution by displacement reaction using zinc.



This process is called Mac - Arthur Forest Cyanide process. Gold obtained by any of the processes is impure and is found mixed with metals like Ag, Cu, Pb and Zn. The refining or parting of the impure gold is accomplished by boiling impure gold with conc. H_2SO_4 . Silver, copper and other metals react with H_2SO_4 forming soluble salts while gold remains unaffected. Nitric acid can also be used for the parting process. At times, electrolysis method is also employed by using an acidified solution of gold (III) chloride, AuCl_3 .

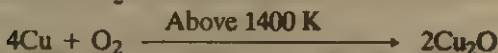
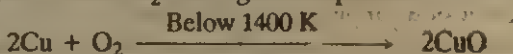
15.5.2 Properties of Copper, Silver and Gold

Copper is a reddish brown metal; silver is a white metal; and gold is a yellow soft metal. Copper, silver and gold are heavy, lustrous, malleable, ductile and good conductors of heat and electricity. The polished surface of silver serves as a very good reflector of light. They, together with platinum metals, are known as noble metals because they are among the chemically most inert metals. They lie below hydrogen in the electrochemical series, and hence, are not capable of displacing hydrogen from acids, water or alkalis.

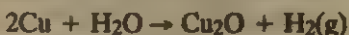


Their reactivity follows the order : $\text{Cu} > \text{Ag} > \text{Au}$

1. **Action of air :** Silver and gold are not affected by air; in moist air, a thin brown layer of oxide or sulphide deposits. On prolong weathering, copper gets covered with a green layer of basic carbonate, $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (verdigris). On heating in air, copper oxidizes to CuO alongwith some Cu_2O at higher temperature.

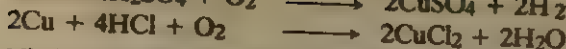


2. **Action of water:** Silver and gold do not react with water. Steam is decomposed by copper at white heat temperature.

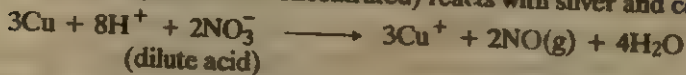


3. **Action of halogens:** F_2 , Cl_2 and Br_2 form dihalides with copper and iodine gives CuI . Both Ag and Au combine with chlorine on heating and produce AgCl and AuCl_3 . On careful heating AuCl_3 decomposes to AuCl . Other halogens also react with both Ag and Au.

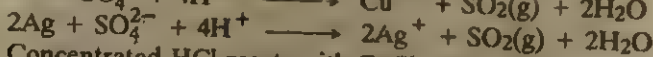
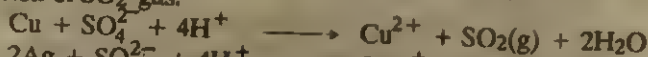
4. **Action of acids:** Non-oxidizing hydrohalic (HX ; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) and dilute sulphuric acids do not react with these metals. They react with copper only in the presence of oxygen (Ag and Au do not react).



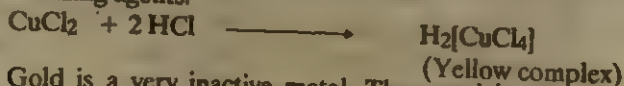
Nitric acid (dilute and concentrated) reacts with silver and copper



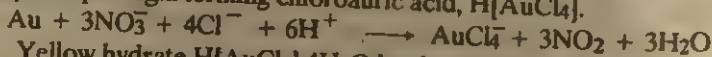
Hot concentrated sulphuric acid reacts with Cu and Ag with evolution of SO_2 gas.



Concentrated HCl reacts with CuCl_2 and AgCl in the presence of some oxidizing agents.



Gold is a very inactive metal. The metal is not attacked by any commonly known single acid. HF reacts very slowly. Gold dissolves readily in aqua regia forming chloroauric acid, $\text{H}[\text{AuCl}_4]$.

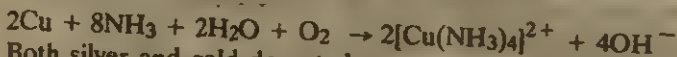


Yellow hydrate $\text{H}[\text{AuCl}_4] \cdot 4\text{H}_2\text{O}$ has been isolated.

5. Action of alkalis : These metals are not attacked by alkalis.

6. Action of hydrogen sulphide : Gold is not affected by H_2S gas. Pure H_2S (a weak acid) reacts with Cu and Ag forming sulphides. Silver is not attacked by oxygen of the air. Air containing H_2S or food materials containing sulphur tarnish the surface of copper and silver. This tarnishing is not the result of a simple reaction between metal and H_2S . Metals could not reduce H^+ ions since they are much below hydrogen in the electrochemical series

7. Action of ammonia : Aqueous ammonia, in the presence of air, dissolves copper. A blue solution containing $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is produced.



Both silver and gold do not show any reaction towards ammonia.

Copper on heating with NH_3 produces interstitial compound, Cu_3N .

8. Action of ozone: Ozone tarnishes copper and silver surfaces. Gold remains unaffected.



9. Displacement Reactions: These reactions depend upon the position of metals in the electrochemical series. According to their position copper is the most electropositive and gold is the least electropositive. Hence, copper can displace both silver and gold from their salt solutions. Silver can displace gold from its salt solutions.



Some typical reactions of copper and Cu^{2+} ions are summarized in

Fig. 15.11.

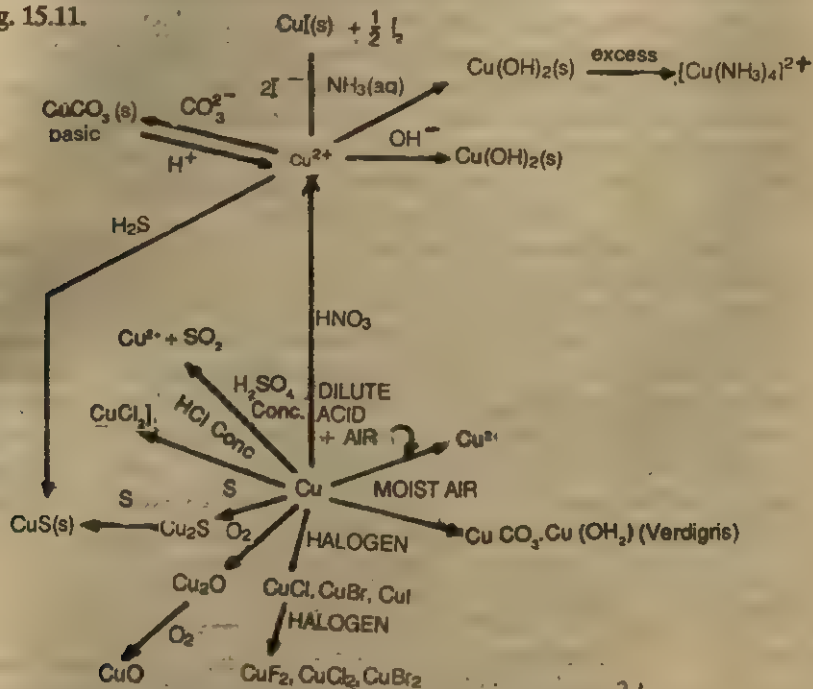


Fig. 15.11. Some typical reactions of copper and Cu^{2+} ions.

15.5.3 Uses of Copper, Silver and Gold

Copper : Copper finds many uses which are listed below :

Stability (inertness) of copper in air and water together with its conducting characteristics could make possible to employ it for various purposes, e.g., (i) since copper is a good conductor of electricity, it is used for manufacturing electrical instruments, goods transmission wires, cables, etc., (ii) the high thermal conductivity of copper leads to its use in making vacuum pans, heating utensils, steam engine boilers, calorimeters and conducting coils, fire boxes of locomotive engines, pipes and radiators used in central heating systems, etc., (iii) the resistance to corrosion makes copper useful for water pipes, (iv) in making coins, (v) in the electrotyping for the printing of books, (vi) in copperplating of some metallic goods, (vii) for producing various alloys (Table 15.4), (viii) several compounds of copper are used in agriculture as insecticides. Bordeaux mixture (copper sulphate mixed with slaked lime) is a well

known spray for fruit trees (fungicide). Another insecticide, **Paris green** (copper arsenite, $\text{Cu}_3(\text{AsO}_3)_2$ + copper acetate) is also employed for the purpose.

Silver : Silver is used: (i) for preparing jewellery, table wares, coins, mirrors and occasionally electric wires. (ii) for preparing silver salts which are used in silver plating of certain metallic wares. (iii) in producing its salts, e.g., halides and nitrates. (iv) in photochromic glass (darkens on exposing to light and shines in darkness). (v) used for electrical conductors and contact points as it does not get oxidized on being heated in air. (vi) for producing various alloys (Fig. 15.4); silver amalgams in filling teeth; used in parts of rockets and missiles and in electronic devices. (vii) for medicinal purposes. (viii) for preparing silver nitrate. It is used in the preparation of light sensitive photographic emulsions. It is an essential laboratory reagent.

Gold : Gold is used : (i) in jewellery, dental fillings and coins (gold coins are no longer in wide circulation). The purity of gold is expressed in carat. 24-carat gold is 100% pure. Jewellery is made out of 22-carat gold (22 parts of gold and 2 parts of copper or silver). (ii) for covering temple domes because it is very inert to weathering processes. (iii) in the form of colloidal gold (**purple of Cassius**) to make red stained glass or porcelain. (iv) as suspensions in galvanometers (gold is good conductor of electricity and can be drawn into an extremely fine wire). (v) in gold plating the base metals. (vi) for providing electrical contact in computers. (vii) in electronic and space applications. (viii) for producing gold alloys.

TABLE 15.4 Alloys of copper and silver

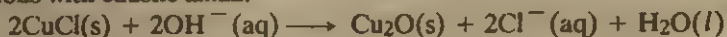
Name	Composition	Uses
Brass	Cu 70%, Zn 30%; Cu 60%, Zn 40%	Cartridge caps, ship fittings, utensils, condenser tubes, sheets etc
Bronze	Cu 70-95%, Zn 1-25%, Sn 5-10%	Fittings, statues, coins and control valves.
Aluminium bronze	Cu 90%, Al 10%	Golden yellow colour - used for paints, cheap jewellery and coins.
Bell metal	Cu 80%, Sn 20%	Bells, gongs, etc
Monel metal	Ni 60%, Cu 33%, Fe 7%	Marine shafts, vats for chemicals and foods, acid pumps, vessels for carrying out reactions etc.
Phosphor bronze	Cu 95%, Sn 4.8%, P 0.2%	Spring wires, suspension filaments for electrical instruments.
German silver	Cu 25-50%, Ni 10-35%, Zn 25-35%	Wares, resistance wire and coils.
Nickel coin	Cu 75%, Ni 25%	Coins, wares
Silver sterling	Ag 92.5%, Cu 7.5%	Silverwares and jewellery
Silver coin	Ag 90%, Cu 10%	Coins, wares
Gold 18-Carat	Au 75%, Cu 5-15%, Ag 10-25%	Jewellery
Gold 12-Carat	Au 50%, Cu 35%, Ag 15%	Jewellery

15.6 COMPOUNDS OF COPPER, SILVER AND GOLD

All the three metals exhibit an oxidation state of +1 in their compounds. These compounds are largely ionic. The stable and principal oxidation states of Cu, Ag and Au are +2, +1 and +3 respectively. The high ionization potential energies impart considerable covalent character in the compounds of this group. With gold, the Au^{3+} is not formed but this state is possible in the complexes.

15.6.1 Oxides

Monoxides : Monoxides of the general formula M_2O have been well characterized. They can be precipitated by treating their salt solutions with caustic alkali.



It becomes increasingly difficult from $\text{Cu} \rightarrow \text{Ag} \rightarrow \text{Au}$ to obtain them free from water. Anhydrous copper (I) oxide is obtained from aqueous solution whereas gold (I) oxide is precipitated as a hydrate and any attempt to dehydrate this lead to decomposition with loss of oxygen.

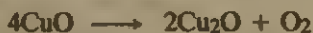
Cu_2O is a reddish brown solid; Ag_2O is a dark brown amorphous solid. Silver (I) oxide can also be formed when silver is exposed to ozone or when finely divided silver is heated in oxygen under pressure. Both Cu_2O and Ag_2O are slightly soluble in water giving alkaline solution. Ag_2O gives a more basic solution. The thermal stability of the monoxides decreases from Cu_2O to Au_2O .



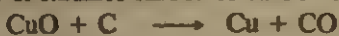
Dioxides : In the divalent state, copper (II) oxide is well characterized, silver (II) oxide is less well characterized and Au (II) oxide is known. Copper (II) oxide is a black insoluble compound. It can be obtained either by direct oxidation of the metal or by heating the hydroxide, nitrate or carbonate.



It is weakly basic in nature. It decomposes to Cu_2O and oxygen at 1173K.



Because of this type of reduction to +1, hot copper (II) oxide is a good oxidizing agent. It oxidizes carbon to carbon dioxide.

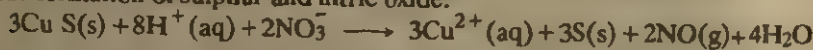


This reaction is used to estimate the percentage of carbon in the organic compounds. Carbon dioxide produced is absorbed in sodium hydroxide, and the gain in mass of the sodium hydroxide is correlated with the carbon content of the compound.

15.6.2 Sulphides

Sulphides in the +1 oxidation state are more stable than +2 state. Copper sulphide, CuS and Silver (I) sulphide, Ag_2S , are precipitated as black solid when H_2S is passed through their aqueous salt solutions in the presence of acid. Gold (I) sulphide is well characterized. In this compound, Au^+ is the most stable. It is formed by passing H_2S gas through an acidified solution of potassium aurocyanide solution, $\text{K}[\text{Au}(\text{CN})_4]$. It is a brown solid, insoluble in water and not attacked by mineral acid. Au_2S_3 is also obtained when H_2S is passed through cold solutions of AuCl_3 in dry ether. Au_2S_3 is readily reduced to Au^+ or the metal on addition of water.

Copper (II) sulphide readily dissolves in warm dilute nitric acid with the formation of sulphur and nitric oxide.



It also dissolves partially in solutions of alkali sulphides. On strong heating Cu(II) sulphide decomposes.



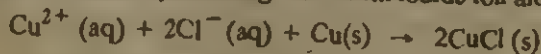
15.6.3 Halides

Table 15.5 includes the known halides of Cu, Ag and Au.

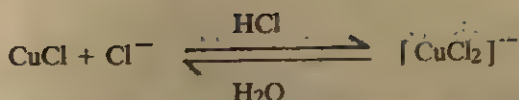
TABLE 15.5 Halides of Cu, Ag and Au

Oxidation state	Fluorides	Chlorides	Bromides	Iodides
+5	AuF_5	—	—	—
+3	AuF_3 (orange yellow)	AuCl_3 (red)	AuBr_3 (red brown)	AuI_3
+2	CuF_2 (white) AgF_2 (brown)	CuCl_2 (yellow brown)	CuBr_2 (Black)	(CuI_2)
+1	— AgF (yellow)	CuCl (white) AgCl (white) AuCl (yellow)	CuBr (white) AgBr (pale yellow) (AuBr)	CuI (white) AgI (yellow) AuI (yellow)

Monohalides : Copper (I) chloride and bromide are prepared by the reduction of Cu^{2+} by reagents such as metallic copper (copper turnings), SO_2 or SnCl_2 in the presence of suitable halogen hydricid. The iodide is obtained by reducing Cu^{2+} with iodide ion alone.



The white crystalline solid of Cu(I)Cl is obtained when the reaction solution is poured into air free distilled water. It is separated, washed and sealed in the absence of air or it soon gets oxidized to CuCl_2 . Copper (I) chloride is soluble in conc. HCl forming the complex ion.



On adding water, Cu(I)Cl reprecipitates. It is used in combination with NH_4Cl as a catalyst in the manufacture of synthetic rubber.

All the four silver (I) halides are known. They are all covalent in nature. All of them can be prepared directly from the elements but it is more convenient to prepare AgF by dissolving Ag_2O in hydrofluoric acid and evaporating the solution until the crystals appear. They can also be prepared by adding X^- to the solution of AgNO_3 or other Ag^+ salts, when AgX is precipitated. They are sensitive to light. Silver bromide is used in photography.

Halides of silver exhibit a series of family trends, both in solubility and in colour. The solubility decreases regularly with increasing molecular mass (AgI is insoluble). The colour intensity increases from AgF to AgI .

AgF (colourless)	AgCl (greyish)	AgBr (canary or pale yellow)	AgI (yellow)
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The colour of silver halides and their solubility in ammonium hydroxide (or in aqueous ammonia) make the basis of their detection in qualitative analysis. AgCl is soluble in aqueous ammonia due to complex formation.



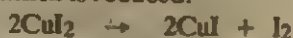
The precipitate reappears on adding dilute HNO_3 . Silver bromide is sparingly soluble in aqueous ammonia whereas silver iodide is insoluble.

Gold, like copper, forms three monohalides. AuF is unknown. Disproportionation occurs in water to Au^{3+} and metallic gold for the chloride and bromide. AuI is stable in water and resembles CuI in this respect. Both AuCl and AuBr are obtained by heating the trihalides to 423K and AuI by heating the metal and iodine.

Dihalides : All the divalent copper halides are known. They are covalent in character. Except CuI_2 , all are stable and can be obtained by heating the finely divided copper metal in the atmosphere of dry halogens. Both chloride and bromide are very soluble in water and various hydrates and complexes can be obtained in crystal forms. Their solutions are obtained by dissolving metal or $\text{Cu}(\text{OH})_2$ in corresponding hydrohalic acids. The colour of concentrated solution of CuCl_2 is dark brown which changes on diluting with water to green and finally to blue.

Blue crystals of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, (a dihydrate of CuF_2) is obtained by dissolving CuCO_3 or CuO in 40% HF .

CuI_2 has not been isolated. Iodide ions reduce Cu^{2+} to Cu^{1+} . In fact Cu(II)I_2 disproportionates, one of iodide ions being oxidized at the expense of the copper, which is reduced.



Silver (II) halides are unknown except AgF_2 which may be obtained by fluorination of silver or silver salts.

All the four halides of Au^{III} are known, the stability decreasing from AuF_3 to AuI_3 . Both chloride and bromide are obtained by direct combination of the metal (gold leaves or finely divided gold) and dry halogens at about 573K. They exist as dimer (Au_2X_6 , $\text{X} = \text{Cl}, \text{Br}$) in the solid as well as in the vapour phase. Both decompose to halogen and gold (I) halide.

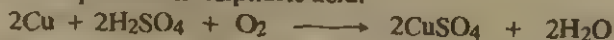


AuF_3 is obtained by the fluorination of gold with BrF_3 . The iodide may be obtained by the reaction between $\text{K[AuCl}_4]$ and conc. KI solution.

15.6.4 Copper Sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

The sulphate is the most common and important of all the copper salts.

It is prepared industrially either by blowing a stream of air through scrap copper and dilute sulphuric acid or by oxidizing sulphide directly to sulphate. Sometimes sulphide is first roasted to oxide which may later be converted to sulphate with sulphuric acid.



On recrystallization from aqueous solution, the blue pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (anhydrous salt is colourless) known as blue vitriol (commercial name), is formed.

Properties : The four waters of crystallization of the pentahydrate sulphate are coordinated square planarly to the central copper cation and the fifth water molecule is held by hydrogen bonds between a sulphate ion and a coordinated water molecule. (Fig. 15.12). The blue crystalline pentahydrate on heating loses water in stages and finally anhydrous salt decomposes on strong heating.

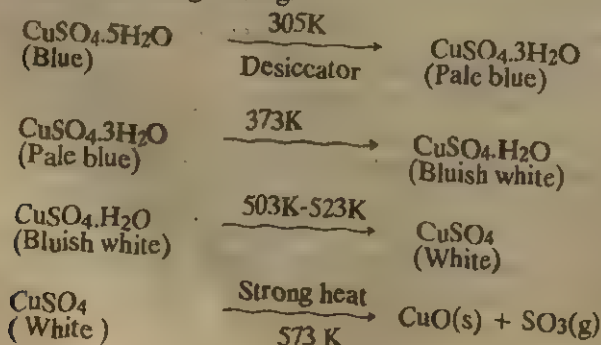
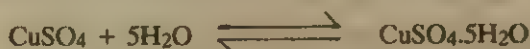


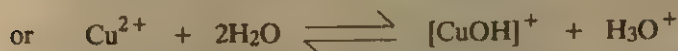
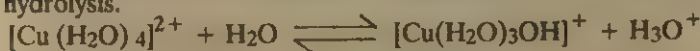


Fig. 15.12. Structure of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ OR $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$

The last water molecule (attached to the SO_4^{2-} ion) is difficult to remove as it is deeply embedded in the crystal lattice. The anhydrous salt, CuSO_4 , gets back its blue colour when treated with water. Thus, dehydration of copper sulphate is a reversible process. This property is employed to ascertain the presence of moisture.

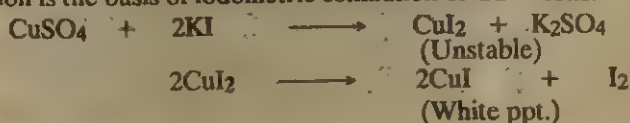


Aqueous solution of copper sulphate shows acidic properties due to hydrolysis.



$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ions impart blue colour to the aqueous solution. Colour, however, depends on the nature of ligands. The colour changes to dark blue colour when water molecules are substituted by NH_3 . Thus, dark blue colour of the solution is due to $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ions or $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$. It also forms double salts with alkali metal sulphate and ammonium sulphate, e.g., $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{K}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 6\text{H}_2\text{O}$.

It reacts with iodides with liberation of iodine quantitatively. This reaction is the basis of iodometric estimation of Cu^{2+} ions.

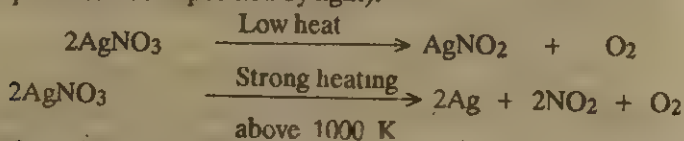


Uses: Copper sulphate is used: (i) in electroplating, in calico-printing, in dyeing, in electrotyping, in the electrolytic refining of copper, in the manufacture of pigments, as a mordant in the textile industry, in the Daniel cell and to prevent the growth of weeds in reservoirs and swimming pools. (ii) as a fungicide and germicide (Bordeaux mixture). Bordeaux mixture, a well known spray for fruit trees and potatoes crop, is a mixture of copper sulphate and slaked lime. (iii) as a starting material for other compounds of copper, (iv) in the form of anhydrous salt to detect water in liquids such as alcohol, ether, etc. Anhydrous salt is used as a dehydrating agent.

15.6.5 Silver Nitrate, AgNO_3

Silver nitrate, known as lunar caustic, is one of the most important soluble salts of silver. It is generally obtained by dissolving silver metal in nitric acid. On concentrating the solution, crystals of AgNO_3 are deposited. It is obtained as an important by-product in the refining of gold by 'Parting process'. For refining purposes impure gold is heated with nitric acid; silver and other impurities (e.g., copper) associated with the gold dissolve leaving behind gold (in a finely divided state) unaffected. Gold powder, thus obtained is melted to get buttons of gold (commercial name 'vitur'). On concentrating and cooling the solution, crystals of impure AgNO_3 are obtained. By taking advantage of thermal instability of $\text{Cu(NO}_3)_2$ (controlled heating), pure sample of AgNO_3 is produced. Impure sample is heated carefully when $\text{Cu(NO}_3)_2$ decomposes producing CuO . The residual mass on dissolving gives an aqueous solution of AgNO_3 . CuO gets separated as insoluble mass. From the solution, pure plates (m.p. 495K) of AgNO_3 are obtained.

Silver nitrate is not very stable and decomposes even on low heating (susceptible to decomposition by light).



Organic compounds such as formaldehyde or sodium potassium tartarate readily reduce alkaline solution of silver nitrate to give free silver, and thus, producing a black stain called 'silver mirror'. Skin becomes black in the contact of AgNO_3 as it gets reduced. Many of the compounds of Ag(I) are insoluble in water and are coloured. AgNO_3 is the only simple and, highly soluble silver salt. It is used in detecting many ions in qualitative analysis.

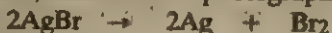
Uses : Much of silver nitrate is used in the preparation of photographic materials, as a laboratory reagent and in the manufacture of other silver compounds. Its use as a caustic depends upon its oxidizing nature. It is used in the dentistry to fill tooth cavities. In the contact of

teeth, it is readily reduced to a black layer of free silver which forms a good junction between tooth enamel and the metallic filling. Its dilute solution is used to cauterise wounds, as an antiseptic for the eyes and for throat infections. It is widely used in silvering of mirrors, as marking ink for clothes, in hair dyes and in silver plating baths as an electrolyte. It is used in qualitative analysis for detecting anions and cations - and in the volumetric estimation (precipitation titrations) of halides and cyanides.

15.7 PHOTOGRAPHY

The process of producing pictures by using light images is called 'photography'. A photograph is the permanent record of images formed on a light sensitive surface.

Photochemical decomposition of silver halides, particularly silver bromide, is the basis of photographic process.

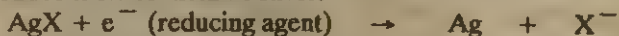


It involves the following essential steps.

1. **The Photographic Films:** Photographic films made of cellulose acetate are coated uniformly with a colloidal suspension of small, silver bromide crystals in gelatin. The size of the silver halide particles and the relative amounts of silver bromide and iodide used determine the sensitivity or 'speed' of the film.

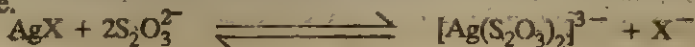
2. **Exposure:** The camera loaded with a film is operated, when the shutter of the camera opens for a moment. This step is called exposure of the film. During exposure, the image of the object falls upon the light sensitive photographic emulsion on the film. The silver halide crystals become 'activated' when exposed to light (from the lighted areas of the object) and undergo photochemical decomposition (reduction) producing silver atoms. This process is called photosensitization. Exposure causes no visible change in the appearance of the film.

3. **Developing:** After exposure, the camera is unloaded and the film is developed in the dark by placing it in a developer which acts as a reducing agent. The developer used for the purpose is an alkaline solution of quinol (hydroxyquinone) or pyrogallol. The reducing agents penetrate the gelatin and reduce the sensitized grains of silver halide with a speed proportional to the intensity of the illumination during exposure and reduce them to metallic silver.



During developing the exposed parts of the film become dark. The unexposed region of the film still continue to be photosensitive, and thus, to avoid the blackening of the film completely, the developing is done in the dark.

4. **Fixing:** After developing, the film is fixed by dipping it into sodium thiosulphate (hypo) solution which dissolves the unreacted silver halide.



This process is also done in dark. The film is now washed with water and left to get dry. Now the film is ready for taking in daylight. The metallic silver remaining on the film forms the visible image and is called a 'negative', since the bright part of the object are now dark and the dark part of the object are now light.

5. Printing: The process of printing is the same as that of making a negative. Now the light is allowed to fall on the sensitive photographic paper (contains AgBr) through the negative. The image is now reversed and dark regions on the negative subsequently become the light regions on the printing paper and vice-versa. The print is now developed and fixed in a way employed for making negative.

15.8 ZINC AND MERCURY

Zinc (Zn), cadmium (Cd) and mercury (Hg) belong to group 12 of the periodic table. These metals have $(n-1)d^{10} 4s^2$ outer electron configuration. With their electronic configurations it is not justified to classify them as transition elements because the completely filled d orbital is not involved in bonding. These metals resemble copper, silver and gold in having completely filled d orbitals in the penultimate shell but are comparatively more active. In their compounds +2 oxidation state is very common which is formed by losing ns^2 electrons. The existence of +1 oxidation state has been well characterized in the case of mercury but it does not exist with either zinc or cadmium. Despite the stability of inner d^{10} core, complexes with 4-coordinate and 6-coordinate numbers are very common.

Unlike transition metals, zinc and cadmium have much in common (occur together in nature and their chemistry is almost identical). These metals are better reducing agents (Unit 10) than coinage metals inspite of the fact that they have much higher ionization potentials. The physical characteristics of these elements are given in Table 15.6.

Reactivity decreases down the group, i.e., $Zn > Cd > Hg$ (electrode potential values). It is interesting to note that although Zn and Cd displace hydrogen from acid but mercury remains unattacked. Mercury is also unique in that it forms mercurous ions each of which contains two mercury (I) ions in covalent combination ($Hg^+ \cdots Hg^+$) or Hg_2^{2+} . These ions are relatively stable in compounds and in aqueous solutions. Mercury exhibits a few characteristics:

1. It is a liquid at ordinary temperatures,
2. It forms amalgams.
3. Its ionization potential is comparable with that of radon, indicating the inert behaviour of s electrons in valence shell.

Like copper, zinc has been known since early times. There are evidences which establish that ancient man used cooking utensils and many other articles made of an alloy of zinc and copper.

Mercury has also been known to the ancients. Aristotle referred this metal as 'liquid silver' or 'quick silver' because of its appearance and

TABLE : 15.6 Physical properties of the elements.

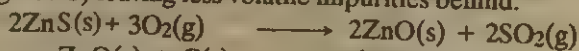
Properties	Zn	Cd	Hg
Atomic number	30	48	80
Atomic radius (pm)	125	141	144
Ionic radius, M^{+} (pm)	74	97	110
Density ($gm\ cm^{-3}$)	7.1	8.6	13.6
Ionization potential ($kJ\ mol^{-1}$)	1st	876	1007
	2nd	1631	1810
Melting point (K)	693	593	235
Boiling point (K)	1180	1040	630
Electrical potential E° (V)	-0.76	-0.40	+0.80
$M^{+2} + 2e^{-} \longrightarrow M$			
Oxidation states	+2	+2	+1, +2
Abundance in earth's crust (ppm)	132	0.15	0.5

liquid state. Its name originated, because of its mobility, after the messenger of the gods in Roman mythology. Its symbol, Hg is derived from hydrargyrum (Latin word means liquid silver). The alchemists made use of mercury in their effort to convert base metals to gold, assuming that it had distinct powers due to its liquid nature. From its ores, gold has been extracted.

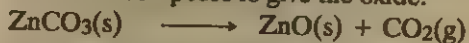
15.8.1 Occurrence and Extraction

Zinc : Zinc is not found in free state in nature. The important ores of zinc are: zinc blende, ZnS ; calamine, $ZnCO_3$; and zincite, ZnO . In India, zinc is mined chiefly as zinc blende from Zawar mines located near Udaipur (Rajasthan).

1. Sulphide ore is first concentrated by froth flotation process and is then roasted at 1175K to form the oxide and sulphur dioxide. Here, some zinc sulphate is also obtained which decomposes at the reaction temperature to give the oxide. Zinc is reduced by coke and being a volatile metal, zinc can be distilled from the reduction furnace, (fire clay retort) (Fig. 15.13) leaving less volatile impurities behind.

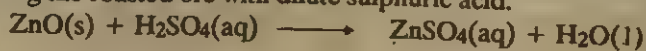


To extract zinc from calamine, it is heated strongly in the absence of air when it decomposes to give the oxide.



Generally zinc is contaminated with cadmium, iron, lead, etc., and it must be fractionally distilled. Zinc can also be purified by electrolytic refining process.

2. Zinc is also manufactured by electrolysis of zinc sulphate. Zinc sulphate is obtained either by roasting the concentrated sulphide ore or by leaching the roasted ore with dilute sulphuric acid.



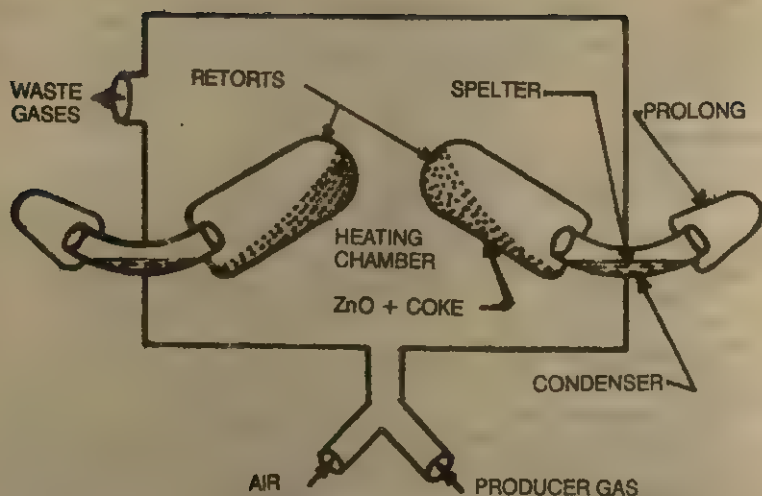
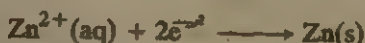
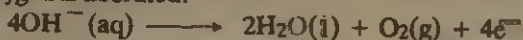


Fig. 15.13. Reduction of zinc; an assembly of a Belgian process.

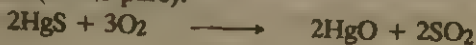
During electrolysis very pure zinc is deposited on aluminium cathode



It is then removed by scrapping. It is 99.95% pure. At the lead anodes, dioxygen is liberated.



Mercury : Elemental mercury is, at times, found in rocks. However, the only important ore of mercury is the dark red sulphide, HgS , known as cinnabar. It is found along lines of volcanic activity. Extensive deposits (6 – 7% Hg) of cinnabar are found at Almaden in Spain. Its other deposits, usually containing less than 1% Hg are found in USSR, Mexico, Algeria and Italy. Cinnabar (concentrated by froth flotation process) on roasting gives thermally unstable oxide which decomposes at the temperature of furnace. Ore itself reduces the oxide to mercury. Metallic mercury distills from the furnace and is condensed to the liquid state (99.7% pure).



The reduction is carried out in a shaft furnace (Fig. 15.14) attached with condensation chambers. Mercury obtained from the chambers contains lead, zinc and tin as impurities. It could be purified by filtering through chamois or a gold seal. The mercury 'wets' the gold seal and passed through it; the impurities are left behind. It can also be purified by passing it slowly through dilute HNO_3 to oxidize the metallic

impurities. Some mercury is converted to $\text{Hg}_2(\text{NO}_3)_2$ which reacts with the metallic impurities forming pure mercury. Mercury is best purified by distilling it in the atmosphere of oxygen to separate the more active metals.

15.8.2 Properties of Zinc and Mercury

Zinc and cadmium exhibit many common features in their chemistry but they differ markedly from mercury. All the three metals are silvery in appearance and volatile. Zinc is a bluish white metal which has a lower melting and boiling points than the transition metals. It has a high tensile strength and is a good conductor of heat and electricity. It has excellent resistance to atmospheric corrosion.

Zinc is more reactive than mercury. As compared to zinc, mercury has relatively low thermal and electrical conductivity. Mercury is a liquid

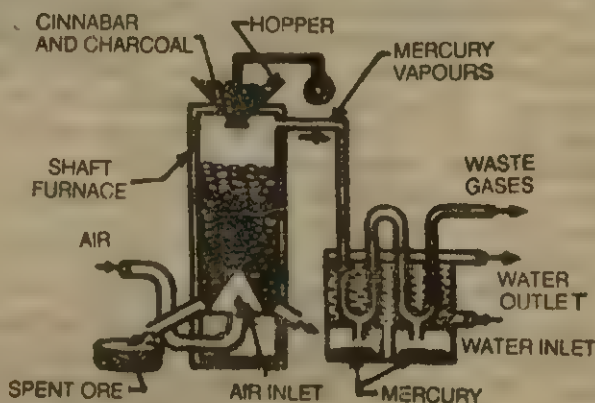
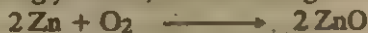


Fig. 15.14. Shaft furnace for the extraction of mercury

at low temperature due to the weak interatomic forces. Mercury vapours are highly toxic and poisonous in nature. Mercury is slightly soluble in water. Its solubility seems to enhance its poisonous nature. Hg^{2+} ions combine with the tissues of kidney and destroy their function of removing waste products from the blood. Egg white and milk act as antidotes because their proteins precipitate the mercury in stomach.

1. Action of air : There is an increasing resistance to the environmental effects. Zinc quickly tarnishes to a blue grey appearance and an adherent coating of basic carbonate $\text{Zn}(\text{OH})_2 \cdot \text{ZnCO}_3$ is deposited which protects the metal from further corrosion. Mercury is not affected at all.

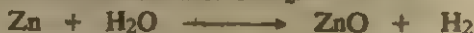
Zinc, when strongly heated, burns forming oxides.



Mercury is slowly oxidized on heating near its b.p. forming HgO . On heating to a higher temperature, it decomposes.

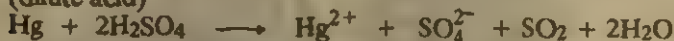
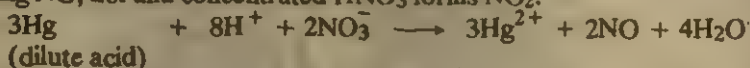


2. Action of water : Mercury is not affected by water even on heating. Zinc reduces boiling water to a small extent. It reacts with steam at high temperatures with liberation of H_2 .



Zinc is not affected by cold water. Granulated zinc is obtained when molten zinc is poured into cold water.

3. Action of acids : Pure zinc is not affected by non-oxidizing acids (HCl or H_2SO_4) but the impure metal dissolves in dilute acids liberating hydrogen (oxides of nitrogen or ammonia with nitric acid). Mercury reacts only with oxidising acids, e.g., nitric acid (dilute and concentrated). Both Hg and Zn are affected by hot concentrated H_2SO_4 . The reaction of Zn and Hg with HNO_3 depends upon the temperature and the concentration of the acid. Dilute and warm HNO_3 reacts with Hg and Zn forming NO ; hot and concentrated HNO_3 forms NO_2 .



In the presence of excess of mercury, Hg(I) salts are obtained.

4. Other reactions : These metals are attacked by halogens and sulphur forming halides and sulphides. Hydrogen and nitrogen react with zinc forming ZnH_2 and Zn_3N_2 . Sulphur powder is generally spread over spilt mercury to prevent poisoning by mercury vapours. HgI_2 , a scarlet red precipitate, on dissolving in KI solution forms a colourless solution of K_2HgI_4 . Its alkaline solution (Nessler's reagent) reacts with ammonia or ammonium salts forming brown coloured solution or precipitate.

15.8.3 Uses of Metals and their Compounds

Zinc : Zinc is mainly used in providing a protective coating on iron sheets (galvanization). In galvanization clean sheet of iron is dipped into or sprayed with molten zinc. Zinc is used in dry cells and for producing alloys (e.g. brass-Cu, Zn). It is also used in zinc plating from a solution containing ZnSO_4 . It has been used in metallurgy of both silver and gold by the cyanide process and in the purification of Ag by Parkes' process. It is used as a reducing agent in the manufacture of perfumes, synthetic drugs and dyestuffs.

Lithopone, a mixture of ZnS and BaSO_4 is used as white pigment. Zinc chloride is employed as a caustic in surgery and as a dehydrating agent in certain organic reactions. A solution of ZnCl_2 (acidic nature)

along with ammonium chloride is used as flux to dissolve coating of oxides on metal surfaces, before soldering. It is also used in preparing fibreboard. A solution of ZnO in ZnCl_2 is used as cement. Zinc white or Chinese white, a white paint, contains ZnO . Zinc oxide is used in the manufacture of automobile tyres, rubber articles and medical ointments.

Mercury : Because of the fact that mercury is an opaque liquid at ordinary temperatures, highly dense, inactive, electricity and heat conductive, it is extensively used in electrical switches, liquid scales and measuring instruments - thermometers, brometers, manometers and high vacuum air pumps. Mercury vapours (conducting nature) are also used in mercury vapour and fluorescent lamps. These lamps under high electrical potential emit bluish-green light, and hence, are used for artificial illumination.

Mercury forms alloys with other metals. These alloys are called amalgams. These can be made available both in the liquid and solid forms. As a result, the reactivity of the amalgamated metal may be enhanced or reduced, e.g., sodium amalgam is less reactive than sodium due to decrease in concentration (dilution effect) and aluminium amalgam is more reactive than aluminium as metal is saved by mercury from being covered by an adherent coating of oxide. Mercury amalgams with Sn, Au, Ag and other metals are used by dentists in teeth fillings. Mercury is used in the extraction of gold and silver by using amalgamation method. It is used as electrode in electrochemical cells for the production of chlorine gas and sodium hydroxide from concentrated brine solution. It is employed as a starting material for preparing its compounds.

Mercurochrome and merthiolate (complex mercury compounds containing organic compounds) are used as antiseptics. Other important applications for mercury include the production of mercurial drugs, detonators (e.g., mercury fulminate, $\text{Hg}(\text{OCN})_2$ is explosive). Mercurous chloride (calomel) is used in medicines as laxative and ointments. Calomel, because of its insolubility, is not poisonous and used as germicides. It is used in calomel electrode. Corrosive sublimate (HgCl_2) and mercury vapours are highly toxic and are used in insecticides and plant sprays.

Black and red sulphides of $\text{Hg}(+2)$ under the name of vermilion have been used as pigment. Vermilion is widely used in cosmetics. It is also used as an Ayurvedic medicine under the name of *Makaradhwaj*. HgO (both red and yellow forms) is used in paint industry. It is also used in medicines for skin diseases. Mercury compounds e.g., HgCl_2 , Hg_2Cl_2 , K_2HgI_4 are used as laboratory reagents.

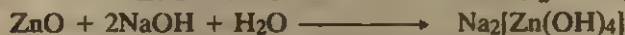
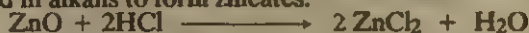
15.9 COMPOUNDS OF ZINC AND MERCURY

Both the metals form compounds corresponding to +2 oxidation state. They are considerably covalent in character. Mercury forms compounds with +1 oxidation state also.

15.9.1 Oxides

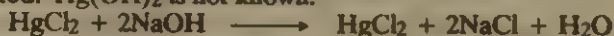
Both Zn and Hg form oxides.

Zinc oxide is produced by burning metal in air or by heating the carbonate or nitrate. It is normally white and becomes yellow on heating due to partial evaporation of oxygen from the lattice. It sublimes on 673K without decomposing. It is amphoteric in nature, dissolves in acids to form salts and in alkalis to form zincates.



Zinc oxide is reduced to metal on heating with carbon or hydrogen. Zinc oxide finds its major use in the production of rubber, where it shortens the time of vulcanization. It is used in the manufacture of glasses, enamels and glazes. Along with chromic oxide, it works as a catalyst in the synthesis of methyl alcohol from water gas and hydrogen. It is a good fungicide. (For its other uses refer to Section 15.8.3).

Mercury (II) oxide exists in a red and a yellow variety. The difference in colour has been attributed to the particle size, the crystal structure being the same in two cases. Red variety is obtained by pyrolysis of $\text{Hg}(\text{NO}_3)_2$ or by heating the metal in air or oxygen at 623K. Yellow variety is obtained by adding alkali to a salt solution. HgO is precipitated. $\text{Hg}(\text{OH})_2$ is not known.



Mercury (II) oxide decomposes on strong heating. The yellow form is slightly metastable with respect to red. It does not react with alkali, but reacts with acids forming salts. It reacts with certain alkali metal halides on heating.



15.9.2 Halides

The known halides of +2 oxidation state are included in the Table 15.7

TABLE 15.7. Halides of Zn and Hg with their m.p. (K)

Flourides	(decompose)	Chlorides	Bromides	Iodides
Zn (+2)	ZnF_2 (1145) (white)	ZnCl_2 (548) (white)	ZnBr_2 (667) (white)	ZnI_2 (719) (white)
Hg (+2)	HgF_2 (918) (white)	HgCl_2 (553) (white)	HgBr_2 (511) (white)	HgI_2 (530) (red and yellow)
Hg (+1)	Hg_2F_2 (843) (yellow)	Hg_2Cl_2 (656) (sublime) (white)	Hg_2Br_2 (618) (sublime) (white)	Hg_2I_2 (413) (sublime) (yellow)

Zinc Dihalides

Diflourides of Zn and Hg are distinct and ionic in nature. Zinc dihalides are, in general, hygroscopic and very soluble in water.

Anhydrous dihalides are prepared by heating the metal in dry Cl_2 (or HCl) Br_2 or I_2 . Aqueous solution of zinc dihalides can be prepared

by the usual methods, e.g., ZnCl_2 can be prepared by the reaction of dilute hydrochloric acid on zinc metal, ZnO or ZnCO_3 . These aqueous preparative methods yield hydrates.

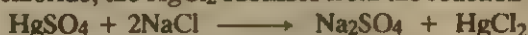
Being covalent in character, the dihalides have low m.p. and dissolve in ethanol, acetone, and other organic solvents.

Aqueous solution of ZnCl_2 is acidic due to hydrolysis. Concentrated aqueous solution of ZnCl_2 dissolves starch, cellulose, and silk forming a gelatinous mass which may be moulded into various shapes. Apart from its uses listed in Section 15.8.3, ZnCl_2 is used in textile processing, and in preserving timbers. It is also used in the preparation of vulcanized paper and fiberboard. It is used as flux in the extraction of metals as well as in the manufacture of magnesia cements for dental fillings.

Mercury Dihalides

Dihalides of mercury are prepared by combining halogens with mercury under proper conditions. They are low melting and volatile covalent solids. Being covalent they are soluble in many organic solvents. They are soluble in water, HgI_2 being only slightly soluble.

Mercury (II) chloride is the most important among all the dihalides of mercury. Apart from the elemental combination, HgCl_2 may be prepared by dissolving mercury (II) oxide in hydrochloric acid or by the action of aqua regia upon mercury. It is manufactured by heating HgSO_4 with sodium chloride; the HgCl_2 sublimes from the reaction mixture.



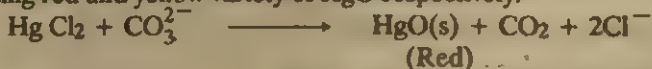
A small amount of manganese dioxide is also added in the reaction mixture to oxidize Hg(I) salt formed during the reaction.

It is a white crystalline solid, moderately soluble in cold water, but soluble in hot water. It dissolves in some organic solvents, such as ethanol and ether (solubility suggests its covalent nature). Its solubility in water is increased by excess of Cl^- ions, which form complex.



Tetra-chloro-mercurate ion

It reacts with sodium carbonate and aqueous caustic soda producing red and yellow variety of HgO respectively.



It is not affected by hot conc. HNO_3 and volatilizes away when treated with boiling conc. H_2SO_4 .

Mercury chloride is readily reduced to Hg_2Cl_2 and mercury on treating with SnCl_2 solution.



Formic acid also reduces HgCl_2 to Hg_2Cl_2 and Hg .

Mercury (II) chloride is hydrolyzed to a small extent by water and ammonolyzed by aqueous ammonia.

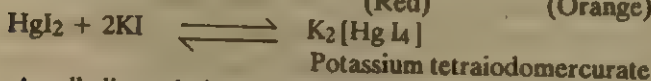
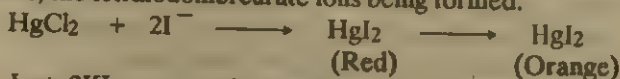


Hydrogen sulphide reacts with HgCl_2 in acidic solution giving a black precipitate of HgS .

In dilute solution, HgCl_2 is used as an antiseptic. It is, however, poisonous in nature. It is called corrosive sublimate. It is used for treating seeds, tanning leather, preparing other mercury compounds for dying fabrics, as a catalyst in organic synthesis and as a disinfectant.

Mercury (II) Iodide

Iodide ions on reacting with HgCl_2 solution, precipitate an orange solid. The precipitate of HgI_2 is soluble in the presence of excess of iodide ions, the tetraiodomercurate ions being formed.



An alkaline solution of $\text{K}_2[\text{HgI}_4]$ is called 'Nessler's reagent' and is used to detect the presence of NH_4^+ ions and ammonia gas.

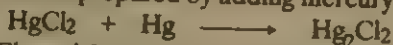
Mercury (I) Chloride and other Mercury (I) Halides

The halides are the most important compounds of mercury with +1 oxidation state (Table 15.7). Hg_2F_2 is prepared by adding HF to Hg_2CO_3 . It dissolves in water but is immediately hydrolyzed to the black oxide (a mixture of Hg + HgO).

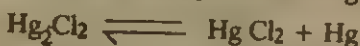
The other halides, Hg_2X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are precipitated from the solution of $\text{Hg}_2(\text{NO}_3)_2$ by adding X^- (in a salt) as they are insoluble in water, e.g.,



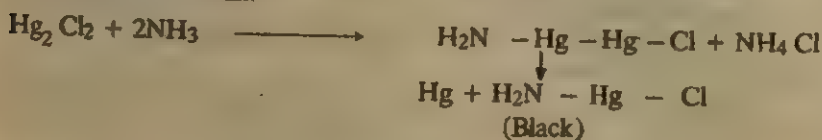
They can also be prepared by adding mercury to HgX_2



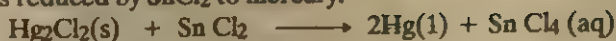
Both Hg_2Cl_2 and Hg_2Br_2 are volatile and can, thus be purified by sublimation. They decompose on strong heating.



Mercury (I) chloride is called 'calomel' (beautiful black) with has originated from the black colour of the precipitate formed by the addition of ammonia and alkali.

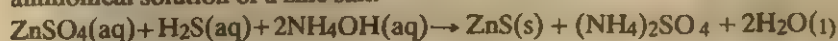


It is reduced by SnCl_2 to mercury.



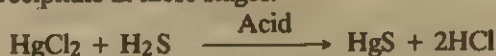
15.9.3 Sulphides

Both zinc and mercury form sulphides. They occur in nature as zinc blende and cinnabar respectively. A colourless precipitate of zinc sulphide is obtained in the laboratory by passing H_2S gas through an ammonical solution of a zinc salt.



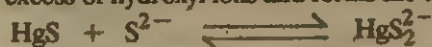
Zinc sulphide dissolves readily in mineral acids with evolution of H_2S gas. Hence, it cannot be precipitated in acidic medium. It turns grey on exposure to light, probably due to the dissociation to the elements. It emits cold light under the action of radiant energy or electrons. This property of ZnS has made it possible to luminescence. This property of ZnS has made it possible to use it in the manufacture of cathode ray tubes and radar screens.

Mercury (II) sulphide is obtained in two forms : (i) black amorphous HgS , and (ii) red crystalline HgS . The black form is usually obtained on passing H_2S gas through an acidic solution of mercury salt. The precipitate so formed is initially white and then becomes yellow, then red and finally black. This is because of the difference in composition of the precipitate in these stages.

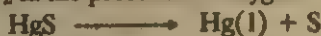


On heating, black HgS sublimes and gives beautiful red coloured HgS known as vermilion. It is insoluble in most of the reagents; it dissolves readily in aqua regia or hydrochloric acid containing potassium chlorate. It is also attacked by conc. HBr and HI .

It dissolves in aqueous solution of sodium sulphide in the presence of an excess of hydroxyl ions and forms the thiomercurate ion.



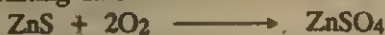
On strong heating, it decomposes to mercury and sulphur, sulphur being converted to SO_2 in the presence of oxygen.



15.9.4 Sulphates

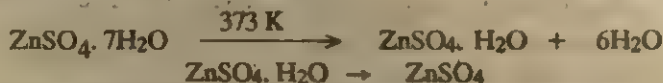
Both Zn and Hg form sulphates.

Zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, known as white vitriol, is manufactured by roasting zinc blende at low red heat.



On a small scale, it is prepared by treating metallic zinc, zinc oxide, or zinc carbonate (calamine) with dilute H_2SO_4 . The product is extracted with water and evaporated to crystallization. Crystals of the heptahydrate $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ are obtained.

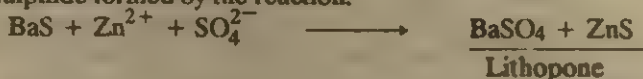
It is isomorphous with other vitriols like $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, etc. and can form mixed crystals with these compounds. On heating to 373K, it loses six water molecules. The seventh water is also lost when it is heated at 723K and becomes anhydrous.



On heating beyond 723 K, it breaks down into zinc oxide.



The compound is very soluble in water. It is used in the production of white pigment, lithopone, which is a mixture of barium sulphate and zinc sulphide formed by the reaction.

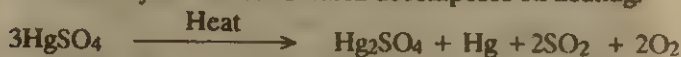


It is used in galvanizing iron and steel. It is used in dyeing, in cotton printing, in medicine and is also the starting material for preparing other zinc compounds.

Mercury (II) sulphate is obtained by the reaction of mercury with conc. H_2SO_4



It is a white crystalline solid which decomposes on heating.



Some important alloys of zinc have been included in Table 15.4 given under Section 15.5.3.

15.10 TIN AND LEAD

Tin and lead belong to group 14 of the periodic table. The first two elements carbon and silicon have already been discussed in Unit 12. The elements of the group have $ns^2 np^2$ electron configuration and form both M(II) and M(IV) oxidation states. As with group 13 elements, the higher oxidation state becomes less stable with increasing atomic number.

Carbon and silicon are primarily non-metallic in nature, while germanium tin and lead become increasingly metallic in properties with increasing atomic number. The metals of this family are reasonably reactive but are frequently protected by a surface coating. Some physical properties of the group 14 elements are given in Table 15.8.

Tin and lead are two of the oldest metals known to man. Tin has been found in Egyptian tombs showing that the metal was known from very early periods of history. Its production dates back to 3500 - 3200 B.C. Lead was used in ancient Egypt for glazing pottery (7000 - 5000 BC); the Hanging Gardens of Babylon were floored with lead sheet to retain moisture.

15.10.1 Occurrence and Extraction of Tin and Lead

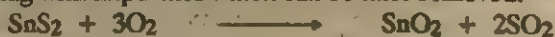
Tin : The most important ore of tin is cassiterite or tinstone, SnO_2 which is found in Malaysia, South America, South Africa and Burma.

TABLE 15.8 Properties of group 14 elements

Property	C	Si	Ge	Sn	Pb
Atomic number	6	14	32	50	82
Atomic radius (pm)	91	132	137	162	175
Covalent radius (pm)	77	117	122	140	154
Ionic radius, M^{2+} (pm)	—	—	093	112	120
Density (g cm^{-3}) (293K)	2.22 (graphite) 3.51 (diamond)	2.33	5.32	7.3	11.3
Ionization potential 1st: KJ mol^{-1}	1086	786.3	761.2	708.4	207.2
2nd:	2351.9	1576.8	1537	1411.4	1450
Melting point (K)	4273	1693	1218	505	600
Boiling point (K)	—	3653	3123	3396	5124
Electrode potential, E° , (V) $\text{M}^{2+} \text{M}$	—	-0.84	-0.30	-0.136	-0.130
Oxidation states	-4, -1	4	4	+2(+4)	+2(+4)
Abundance in earth's crust (ppm)	320	227, 200	7	40	16

In India small amounts of tinstone are found in Hazaribagh (Bihar) and Orissa. Tinstone contains 5-10% of tin as SnO_2 , the rest being impurities consisting of silicious matter, pyrites of iron, copper and arsenic tungstates of iron and manganese called wolframite.

The tin ore is crushed and washed with water to separate the lighter rocky materials from the heavier ore (wolframite and pyrites). The ore is then roasted in a current of air, when sulphur and arsenic are removed as sulphur dioxide and arsenic dioxide, As_2O_3 . Iron and copper pyrites are converted to their oxides and sulphates. These are extracted by dilute HCl and tinstone is left behind as insoluble. It is called 'black tin' and contains 60-70% of tin as tin oxide. The purified ore is reduced by carbon (anthracite) in a reverberatory furnace. Limestone is added to produce a slag with impurities which can be later removed.



Because of the presence of iron in the ore of tin, it is necessary to reduce tinstone/iron oxide at sufficiently high pressure of oxygen to prevent extensive reduction of iron. Metallic iron and tin stone form a hard product, with unacceptable impurities.

The molten tin, called 'black tin', contains 99.5% metallic tin. It is drawn off and cast into ingots or blocks. The crude tin is remelted and the easily fusible tin melts away and less fusible compounds of iron and arsenic and other impurities are left behind. The molten metal is further purified by stirring vigorously in atmosphere of oxygen with long billets of

green wood (poling) to oxidize iron. The impurities are brought to the surface in the form of scum and are skimmed off. This step can also be achieved by using steam or compressed air. Further purification of the tin is accomplished by electrolysis, using impure tin as anode and pure tin cathode. The electrolyte consists of hydrofluorosilicic acid (H_2SiF_6), tin sulphate and sulphuric acid.

Lead : Galena (PbS) is the principal ore of lead, often found associated with zinc blende, ZnS . Other common, but less important ores of lead are the carbonate, cerussite (PbCO_3); and the sulphate, anglesite (PbSO_4) which appear to have been formed by the weathering of sulphide ores. In India, small quantities of lead ores are found at Panjori in Swai Madhopur, Jaipur and Chitral (Rajasthan).

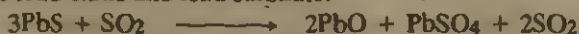
Two methods of extraction are employed :

- (1) Self reduction or air reduction method, and
- (ii) Carbon reduction method.

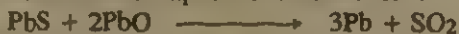
The concentration of the ore is done by a series of selective processes to remove the silicious materials and other sulphides associated with the ores.

Self Reduction or Air Reduction Method

Enriched galena is roasted in a reverberatory furnace. The ore is oxidized to lead oxide and lead sulphate.



Now more of galena is added and the air supply is reduced. The galena reduces the oxide and sulphate to metallic lead.

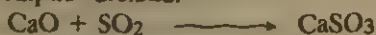


Carbon Reduction Method

The concentrated sulphide ore is mixed with lime and roasted in a sinterer (Fig. 15.15). The roasting takes place in the presence of a blast of air at high temperature. As a result, the sulphides of Pb and Zn are oxidized to oxides.



Lime helps the forward reaction by combining with sulphur dioxide.



The oxides are now mixed with coke, scrap iron and lime (flux) and smelted in a blast furnace. A blast of air necessary for combustion is introduced from

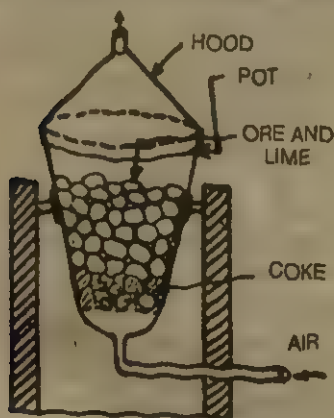
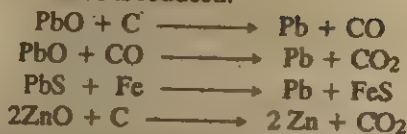
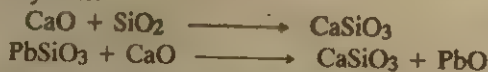


Fig. 15.15 Sinterer for roasting of concentrated ore.

the bottom. The lead oxide is reduced.



Lime removes silica as fusible slag of calcium silicate. Lime does not allow lead to be wasted as lead silicate, PbSiO_3 which even if formed, is decomposed by lime.



Both the molten lead and the slag collect in the lowest part of the furnace known as hearth. The slag floats on the surface of the molten metal and is drawn out through the slag hole while the lead is removed through the tapping hole.

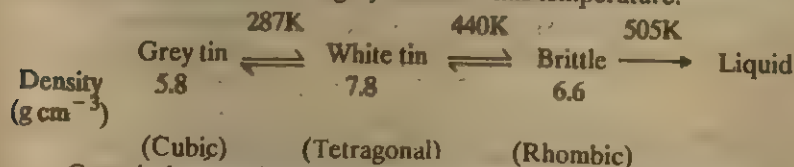
Zinc vapours coming out from the top of the furnace are condensed. Zinc, being less dense than lead, forms the upper layer and can be removed.

Lead prepared by the above methods always contains impurities such as gold, silver, copper, iron, tin and antimony which make the metal hard and brittle. The impure metal is heated in a shallow reverberatory furnace in the presence of air. The oxides of the metals other than Pb rise to the surface and molten lead is drained off for further refining. Gold and silver may be extracted from the lead by the Parkes process or by the electrolytic process - thin sheets of pure lead are made the cathodes, plates of impure lead the anodes, and the electrolyte contains lead hexafluorosilicate (PbSiF_6) and hexafluorosilicic acid (H_2SiF_6).

A recent method of lead extraction involves the electrolysis of lead sulphide dissolved in molten lead chloride.

15.10.2 Properties of Tin and Lead

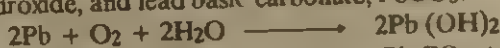
Tin exists in three solid allotropic forms, which differ in their crystal lattice. They are grey malleable and brittle tin. The malleable tin is the ordinary form of tin and is a soft silvery - white, lustrous metal. It is ductile and can be rolled into thin sheets (tin foils). White tin is stable at temperatures above 287K and grey tin below this temperature.



Grey tin has a unique property of catalyzing its own formation. An effect is, thus, produced which, in a way, is similar to the spread of an infection in a plant or animal body. This phenomenon is called 'tin disease'.

Ordinary white tin does not oxidize in air or water at room temperature. But above its melting point, it transforms gradually into tin oxide, SnO_2 .

Lead is a bluish white, heavy and soft metal having little tensile strength. It is the heaviest of the common metals excepting gold and mercury. It has a metallic luster when freshly cut but acquires a dull grey colour when exposed to moist air (moisture + CO_2) due to the formation of lead hydroxide, and lead basic carbonate, PbCO_3 .



Some important reactions of both tin and lead are summarized in Table 15.9

TABLE 15.9 : Reactions of tin and lead

Reagent	Reaction	Comment
1. Oxygen of air	$\text{M} + \text{O}_2 \longrightarrow \text{MO}_2$	Pb is attacked slowly and PbO is formed. Sn is attacked at its m.p.
2. H_2O (room temperature)	$\text{Pb} + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{O}} \text{Pb}(\text{OH})_2$ (soft) (In soft water)	
	$\text{Pb} + \text{H}_2\text{O} \longrightarrow$ Insoluble (Hard) (In hard water)	Sulphate and carbonate present in hard water reacts with $\text{Pb}(\text{OH})_2$ forming insoluble PbSO_4 and PbCO_3
	PbSO_4 and PbCO_3 Sn is not attacked by H_2O	Sn is not attacked by H_2O
3. Steam	$\text{M} + 2\text{H}_2\text{O} \longrightarrow \text{MO}_2 + 2\text{H}_2$	
4. Sulphur	$\text{M} + \text{S}_2 \longrightarrow \text{MS}_2$	Lead forms PbS
5. Chlorine	$\text{M} + 2\text{Cl}_2 \longrightarrow \text{MCl}_4$	Lead gives PbCl_2
6. Aqueous alkali (Hot and conc.)	$\text{Sn} + \text{NaOH} \longrightarrow \text{Na}_2\text{SnO}_2 + \text{H}_2$ $\text{Na}_2\text{SnO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Na}_2(\text{Sn}(\text{OH})_4)$ $\text{Pb} + 2\text{NaOH} \longrightarrow 2\text{Na}_2\text{PbO}_2 + \text{H}_2$ $\text{Pb} + 4\text{KOH} + 2\text{H}_2\text{O} \longrightarrow \text{K}_4\text{Pb}(\text{OH})_6 + \text{H}_2$	Reaction is slow
7. Acids		
(i) Cold and dilute HCl	$\text{M} + 2\text{HCl} \longrightarrow \text{MCl}_2 + \text{H}_2$	Sn reacts very slowly Pb hardly reacts.
(ii) Hot and Conc. HCl	$\text{M} + 2\text{HCl} \longrightarrow \text{MCl}_2 + \text{H}_2$	With Pb slow reaction due to the formation of insoluble PbCl_2
(iii) Hot Conc. H_2SO_4	$\text{Sn} + 2\text{H}_2\text{SO}_4 \longrightarrow \text{SnSO}_4 + 2\text{SO}_2 + 4\text{H}_2\text{O}$ $\text{Pb} + 2\text{H}_2\text{SO}_4 \longrightarrow \text{Pb}(\text{HSO}_4)_2 + \text{H}_2$	Lead reacts vigorously
(iv) Hot Conc. HNO_3	$3\text{M} + 4\text{HNO}_3 \longrightarrow 3\text{MO}_2 + 4\text{NO} + 2\text{H}_2\text{O}$	Lead forms PbO
(v) Dilute HNO_3	$4\text{Sn} + 10\text{HNO}_3 \longrightarrow 4\text{Sn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$ $3\text{Pb} + 8\text{HNO}_3 \longrightarrow \text{Pb}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$	
8. Metals		Forms alloys

15.10.3 Uses of Tin and Lead

Tin : Tin is mainly used in plating iron to resist corrosion. Solid tin is used in the fabrication of stills for the preparation and distribution of distilled water. Tin foils are used for making food containers. It finds use in making alloys (Table 15.10). Tin compounds are used as mordants in dyeing and calicoprinting. Tin amalgam is used for making mirrors.

Lead : Because of its malleability, softness and resistance to corrosion, lead is used in piping and as a roofing material. It is used in storage battery, for covering electric cables, to make bullets and shots. It protects workers handling radioactive materials as it absorbs radiation. It finds use to prepare lead tetraethyl $(C_2H_5)_4Pb$, which is used as an additive to petrol to prevent knocking. It is used to make pigments such as red lead, white lead, chrome yellow and chrome red. Lead chambers are used in sulphuric acid industry. It has been used in manufacturing alloys. (Table 15.10).

TABLE 15.10 Common alloys of tin and lead

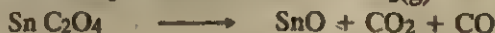
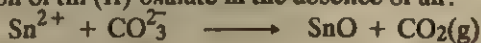
Name	- Composition	Uses
Bronze	Cu 75-95%, Zn 1-25%, Sn 5-10%	Fittings, statues, coins and control valves.
Bell metal	Cu 80%, Sn 20%	For making bells, gongs, etc.
Gun metal	Cu 85%, Sn 5%, Zn 5%, Pb 5%	Gears, guns, castings, bearings, etc.
Phosphor bronze	Cu 95%, Sn 4.8%, P 0.2%	Spring wires, suspension filaments electrical instruments.
Type metal	Pb 70%, Sb 20%, Sn 10%	Printing type
Solder	Pb 67%, Sn 33%	For soldering
Pewter	Sn 90-95%, Sb 1-8%, Cu 0.5-3%	Decorative alloy, making utensils.
Babbitt	(1) Sn 80-90%, Pb 0-5%, Cu 5% (2) Pb 75%, Sn 12%, Sb 13%, Cu 0-1%	In railway wagons, diesel locomotives, etc.

15.11 COMPOUNDS OF TIN AND LEAD

Tin and lead form two series of compounds, corresponding to +2 and +4 oxidation states. Compounds with +4 oxidation state are generally covalent whereas with +2 oxidation state are essentially ionic.

15.11.1 Oxides

Tin Oxides : Depending upon the method of preparation, tin (II) oxide, SnO is a black or green powder. It may be prepared by treating a hot solution of tin (II) oxalate in the absence of air.



The carbon monoxide prevents the oxidation of SnO to SnO_2 .

Amongst the several forms of SnO known, blue-black tetragonal form is the most common. It is amphoteric in nature, dissolving readily in aqueous acids to give $Sn(II)$ complexes and in alkalis to form $[Sn(OH)_3]^-$

Tin (IV) oxide occurs naturally as cassiterite. It is generally obtained when tin is burnt in air or by treating it with conc. HNO_3 . The product is white when cold, but yellow when hot. It is insoluble in water and dilute acids or alkalis but dissolves readily in fused alkali hydroxides to form stannates.



It is amphoteric in nature. It is hydrolyzed by water when a white ppt. of hydrous tin (IV) oxide ($\text{SnO}_2 \cdot \text{H}_2\text{O}$) is obtained which is readily soluble in both acids and alkalis.

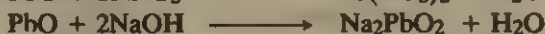
Tin (IV) oxide is used to prepare white glazes and enamels. It finds use as polishing powder.

Lead Oxides : Three oxides of lead are known: $\text{Pb}(\text{II})\text{O}$, $\text{Pb}(\text{IV})\text{O}_2$ and Pb_3O_4 .

Depending upon the method of preparation, lead (II) oxide is red, orange, or yellow in colour. It is prepared by heating lead (II) carbonate, lead (II) nitrate and lead (II) hydroxide.



A yellow variety, a common form, is obtained when molten lead is heated in air. When it is roasted to 773K, it acquires a reddish-yellow colour, and in this form is known as litharge. It is amphoteric in nature.

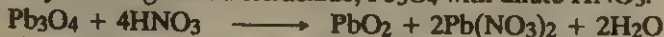


With HCl and H_2SO_4 , insoluble PbCl_2 and PbSO_4 are formed. It is reduced to metal by heating in a stream of hydrogen or carbon monoxide or by heating with carbon.



Lead (II) oxide is used for filling the lead storage battery and in the production of certain grades of glass and paints. It is also the starting material for preparing other lead compounds.

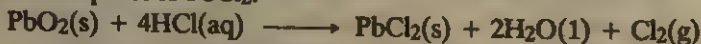
Lead (IV) oxide is a dark brown insoluble solid. It is prepared by oxidizing lead (II) compounds in alkaline solution. It can also be obtained by warming trilead tetraoxide, Pb_3O_4 with dilute HNO_3 .



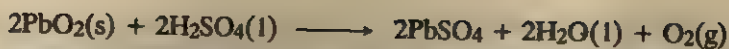
It is amphoteric in nature with acid properties predominating in it. On heating to 573K, it decomposes to oxygen and the lower oxide.



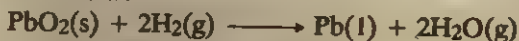
It oxidizes hot conc. HCl to dichlorine. Initially it forms PbCl_4 which decomposes to PbCl_2 .



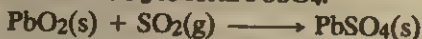
With hot conc. H_2SO_4 , dioxygen is evolved.



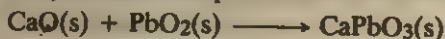
Nitric acid does not react with Pb(IV)O_2 . Similar to PbO , it can also be reduced to metal.



PbO_2 combines with SO_2 to form PbSO_4 .



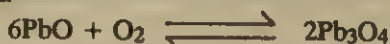
It reacts with alkalis forming plumbates (IV). The fusion of lead (IV) oxide with CaO yields calcium plumbate.



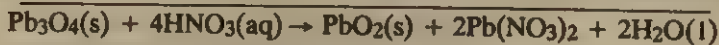
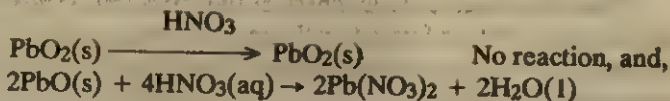
Most plumbates are insoluble in water. Sodium and potassium plumbates are soluble; they are hydrolyzed in solution.

All lead (IV) compounds are strong oxidizing agents. Lead (IV) oxide is used as an oxidizing agent in industries. It is the principal constituent of the cathode of the charged lead storage battery.

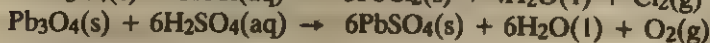
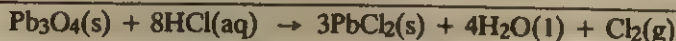
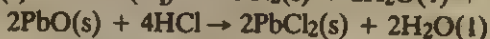
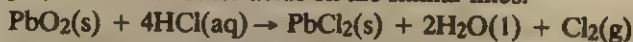
The oxide, Pb_3O_4 , called red lead or trilead tetraoxide is prepared by carefully heating Pb(II) O in air at temperatures between $673\text{K} - 773\text{K}$.



It decomposes above 773K to lead (II) oxide and oxygen. It is a brown solid and behaves as a mixture of PbO and PbO_2 . With dilute nitric acid, the reaction would be expected for a mixture of simpler oxides.



Pb_3O_4 reacts with other acids on the similar lines.



15.11.2 Sulphides

Both SnS and SnS_2 are known. A brown precipitate of Sn(II)S and a yellow precipitate of SnS_2 are obtained when H_2S reacts with an acidic solution of SnCl_2 and SnCl_4 respectively. Sn(IV) S_2 can also be obtained by heating tin shavings with sulphur and ammonium chloride.

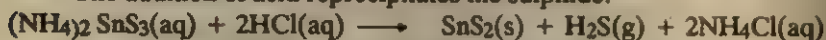
Tin (II) sulphide does not dissolve in alkali metal sulphide and ammonium sulphide, but ammonium and alkali metal polysulphides dissolve it with a formation of thiostannates.



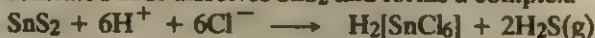
Tin (IV) sulphide dissolves readily in a solution of alkali metal sulphide and ammonium sulphide forming soluble salt of thiostannic acid, H_2SnS_3 .



The addition of acid reprecipitates the sulphide.



Concentrated HCl dissolves SnS_2 and forms a complex.



Lead (II) sulphide is formed as a black ppt, when H_2S reacts with acidic solution of lead (II) salts. This is why a filter paper soaked in a solution of lead (II) salt darkens when it is exposed to H_2S gas. This is used to identify H_2S gas, S^{2-} and $\text{S}_2\text{O}_3^{2-}$ ions. It is insoluble in dilute acid, alkali sulphides and ammonium polysulphide $(\text{NH}_4)_2\text{S}_x$.

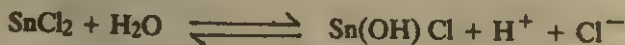
15.11.3 Halides

Tin and lead form two series of halides, MX_2 and MX_4 . Pb(II)X_2 are more stable than Pb(IV)X_4 . The non-existence of PbBr_2 and PbI_2 is attributed to the strong oxidizing properties of lead (IV) salts. Dihalides have greater ionic character in the solid state than the tetrahalides, for instance, their volatility is much less.

Dihalides

Tin (II) fluoride is prepared by evaporating a solution of SnO in 40% aqueous HF . It is used as an ingredient in tooth pastes to decrease dental decay.

Tin (II) chloride is obtained as the dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) by evaporating a solution formed by the reaction of tin or tin (II) oxide with conc. HCl . The salt is hydrolyzed by water forming the basic hydroxy chloride, Sn(OH)Cl .

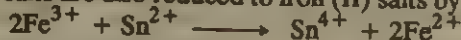


Anhydrous Sn(II)Cl_2 is prepared by heating metallic tin in a current of dry HCl gas.

Tin(II) chloride finds wide use as a reducing agent because of the ease with which tin (II) is oxidized to the tin (IV). It reduces Hg(II)Cl_2 first to white insoluble, Hg_2Cl_2 and then to Hg .



Iron (III) salts are also reduced to iron (II) salts by SnCl_2

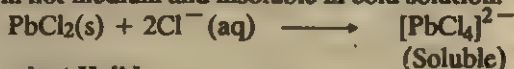


This reaction is the basis of estimating iron (III) salts by redox titrations using KMnO_4 solution.

Tin (II) bromide is a white solid. It forms many hydrates. SnI_2 forms as brilliant red needles. Both SnBr_2 and SnI_2 are prepared when tin is heated with Br_2 in HBr or I_2 in HI .

Lead (II) halides are stable crystalline solids which can readily be prepared by treating any water soluble Pb(II) salt with HX or halide ions to precipitate PbX_2 .

The ionic character of these halides decreases : $\text{PbF}_2 > \text{PbCl}_2 > \text{PbBr}_2 > \text{PbI}_2$ (covalent). All the halides except, PbI_2 which is yellow in colour, are white solids. Lead (II) ions are identified in the qualitative analysis on the basis of colour and insolubility of PbCl_2 and PbI_2 . Both are soluble in hot medium and insoluble in cold solution.



Tetravalent Halides

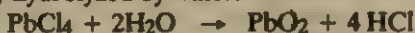
Tin (IV) fluoride is prepared by the action of anhydrous HF on SnCl_4 . It is an extremely hygroscopic and a white crystalline solid which sublimes above 973K. Other SnX_4 are prepared by the direct action of the elements. SnCl_4 is a colourless liquid, soluble in organic solvents, such as CCl_4 and it is covalent in nature.

It is hydrolyzed extensively by water, whereas in HCl (excess) hexachlorostannic acid is produced.



Both SnBr_4 and SnI_4 also hydrolyze readily but definite hydrates can be separated from acid solutions *e.g.*, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $\text{SnBr}_4 \cdot 4\text{H}_2\text{O}$.

Only two tetrahalides of lead, *i.e.*, PbF_4 (yellow crystalline solid) and PbCl_4 (yellow oil) are known. PbF_4 is an ionic solid whereas PbCl_4 is a covalent compound. PbCl_4 is formed as an unstable liquid by reaction between PbO_2 and conc. HCl . It decomposes to PbCl_2 and Cl_2 above 323K. It is readily hydrolyzed by water.



An acidic aqueous solution of PbCl_4 forms complex salt with alkali metal halides; *e.g.*, $\text{M}_2[\text{PbCl}_6]$, $\text{M}_2[\text{PbF}_6]$, ($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Ca}, \text{NH}_4^+$).

SELF ASSESSMENT QUESTIONS

MULTIPLE CHOICE QUESTIONS

Put a (✓) mark against the most appropriate answer :

- 15.1 (i) The molecular formula of Glauber's salt is
 (a) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, (b) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 (c) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (d) $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.
- (ii) Bell metal is an alloy of copper and
 (a) tin (b) aluminium (c) lead (d) nickel
- (iii) Aqua regia is
 (a) 1 part HCl and 3 parts HNO_3 (b) 3 parts HCl and 1 part of HNO_3 (c) 2 parts HCl and 1 part of HNO_3 (d) 3 parts HCl and 2 parts of HNO_3
- (iv) Lead is most readily dissolved in
 (a) H_2SO_4 (b) CH_3COOH (c) HNO_3 (d) HCl

- (v) White lead is
(a) oxide of lead (b) carbonate of lead (c) basic carbonate of lead (d) basic sulphate of lead
- (vi) Which of the following compounds of elements of group 14 would you expect to be most ionic in character ?
(a) PbCl_2 (b) PbCl_4 (c) CCl_4 (d) SiCl_4
- (vii) The purest form of commercial iron is
(a) wrought iron (b) cast iron (c) steel (d) pig iron.
- (viii) In our country iron is obtained from the ore
(a) haematite (b) cryolite (c) azurite (d) cassiterite.
- (ix) Which of the following metals is extracted by smelting ?
(a) sodium (b) calcium (c) copper (d) aluminium
- (x) Which of the following minerals/ores is not an oxide ?
(a) bauxite (b) haematite (c) cuprite (d) calamine
- (xi) Which of the following alloys is an alloy of tin ?
(a) brass (b) magnalium (c) bronze (d) stainless steel
- (xii) The percentage of carbon is the least in
(a) cast iron (b) steel (c) pig iron (d) wrought iron.
- (xiii) Extraction of metals from sulphide ores is accomplished by
(a) froth flotation process (b) smelting process (c) electrolytic reduction (d) thermal decomposition.
- (xiv) A substance used in metallurgy to remove rocky material is called
(a) slag (b) flux (c) oxidizing agent (d) gangue
- (xv) A blast furnace is used in the extraction of
(a) iron (b) zinc (c) aluminium (d) tin.

15.2 Fill in the blanks in the followings:

- (i) An element that can exist as a positive ion in acidic solution and as a negative ion in basic solution is said to be _____. (IIT 1984)
- (ii) The process involved in the production of a metal from its ores are collectively known as _____.
- (iii) The rocky material found with ores is known as _____.
- (iv) The process in which the lighter gangue particles are washed away in a stream of water while the heavier minerals stay behind is known as _____.
- (v) The method of removing volatile matter from ores is known as _____.
- (vi) Roasting is a process in which _____.
- (vii) Hardness of steel is adjusted by _____.
- (viii) In electrolytic refining, pure metal is deposited on the _____.
- (ix) A process of giving a fine coating of zinc metal on iron metal is known as _____.
- (x) Sulphide ores are, generally, concentrated by _____ process.

15.3 Indicate if the following statements are true or false by writing T or F.

- (i) Silver chloride is more soluble in very concentrated sodium chloride solution than water. (IIT 1984)
- (ii) Metals can be recovered from their ores by chemical methods.
- (iii) SnCl_2 is a non-linear molecule.
- (iv) Metals are situated on the right hand side of the periodic table.
- (v) Metals usually occur in the native state in the nature.
- (vi) Bronze is an alloy of copper and zinc.
- (vii) Stainless steel is an alloy.
- (viii) Copper will displace aluminium from its solution.
- (ix) Cast iron is the purest form of commercial iron.

- (x) Bauxite is an ore of aluminium.
 (xi) The electronic configuration of copper is $3d^9 4s^2$.
 (xii) Metals are good conductor of electricity.
 (xiii) The percentage of carbon is 0.2% in wrought iron.
 15.4 Match the descriptions given in column B against the statements/terms under column A.

Column A	Column B
1. Cassiterite	(i) Lead
2. Cerussite	(ii) Silica
3. Calomel	(iii) Hg_2Cl_2
4. Corrosive sublimate	(iv) Zinc
5. White vitriol	(v) $BaSO_4$
6. Lithopone	(vi) $ZnSO_4 \cdot 7H_2O$
7. Calamine	(vii) Iron
8. Limonite	(viii) Tin
9. Malachite	(ix) Copper
10. Flux	(x) $FeSO_4 \cdot 7H_2O$
11. Green Vitriol	(xi) $HgCl_2$

SHORT ANSWER QUESTIONS

- 15.5 State what happens when
1. Aqueous ammonia is added dropwise to a solution of copper sulphate till it is in excess. (IIT 1985)
 2. Tin is treated with conc. HNO_3 . (IIT 1985)
 3. Pb_3O_4 is treated with nitric acid (IIT 1986)
- 15.6 Answer the following questions briefly (IIT 1987)
1. What is the actual reducing agent of haematite in blast furnace.
 2. Give the equations for the recovery of lead from galena by air reduction.
 3. Zinc and not copper is used for the recovery of metallic silver from complex $[Ag(CN)_2]^-$
 4. Why is chalcocite roasted and not calcined during recovery of copper.
- 15.7 (i) Name the ore and the process employed for the extraction of (1) copper, (2) zinc, and (3) iron.
- (ii) Give the chemical reactions which occur in a blast furnace during the extraction of iron from haematite.
- (iii) Give the reaction involved in parting process between Ag and H_2SO_4 as well as Ag and HNO_3 .
- 15.8 (i) Give the reaction which occur when an aqueous solution of $HgCl_2$ is treated with
- (a) an aqueous solution of KI
 - (b) an aqueous solution of $SnCl_2$
 - (c) Copper, and
 - (d) an aqueous solution of NaOH.
- (ii) Copper becomes green when exposed to air for long. Explain.
- 15.9 Complete the following chemical equations.
1. $Na + O_2 \longrightarrow$
 2. $Na_2O + H_2O \longrightarrow$
 3. $2Mg + O_2 \longrightarrow$
 4. $Zn + H_2O \longrightarrow$
 5. $Mg + H_2O \longrightarrow$
 6. $Fe + H_2O \longrightarrow$
 7. $Zn + H_2SO_4 \longrightarrow$
(dilute)

8. $\text{Na} + \text{HCl}$ \longrightarrow
 9. $\text{Cu} + \text{H}_2\text{SO}_4$ \longrightarrow
 10. $\text{Mg} + \text{HCl}$ \longrightarrow
 11. $\text{Al} + \text{HCl}$ \longrightarrow

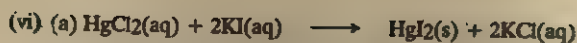
TERMINAL QUESTIONS

- 15.1 What type of ores are roasted? Write a chemical equation for the roasting of an ore of each type. Why is this procedure used?
- 15.2 How will you obtain (i) iron from Fe_2O_3 (ii) copper from copper pyrites and (iii) zinc from zinc blende? Outline the steps involved.
- 15.3 Briefly explain each of the followings: (a) galvanizing, (b) froth flotation process, (c) oxidative refining, (d) leaching and (e) Aluminothermy.
- 15.4 (a) What is steel? Explain the terms: (i) tempering of steel, and (ii) stainless steel.
 (b) The equation: $\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$ represents the changing of iron ore into iron. (i) What compound has been oxidized? (ii) What compound has been reduced? (iii) Explain giving chemical equations, how is carbon monoxide produced in a blast furnace?
- 15.5 (a) List the steps involved in the extraction of zinc from its carbonate ore.
 (b) Give in brief the procedure used for extraction of tin from tinstone.
- 15.6 Describe the extraction of copper from a sulphide ore under the following headings: (i) concentration (ii) roasting (iii) conversion to metal and (iv) electrolytic refining.
- 15.7 (a) State two reactions, if any, of the following metals with a solution of copper sulphate: (i) mercury (ii) iron (iii) zinc (iv) tin.
 (b) Aluminium is more active than iron and yet there is less corrosion of aluminium when both are exposed to air. Explain.
- 15.8 How do the metals copper, zinc, tin and lead react with water and air?
- 15.9 (a) What is the action of common acids on the following metals: iron, copper, zinc, silver, tin, lead and mercury.
 (b) Cupric hydroxide dissolves in excess of ammonia. Comment.
 (c) All the water molecules present in copper sulphate are not alike.
- 15.10 (a) (i) Which one of the followings is acidic flux: SiO_2 or CO ? (ii) Which one of the followings is an alloy of iron: Gun metal or Brass or Duriron? (iii) which one of the followings is capable of forming complexes: Zinc or Magnesium? Explain.
 (b) Explain the following statements:
 (i) Fe^{2+} is oxidized to Fe^{3+} easily but Co^{2+} and Ni^{2+} are not easily oxidized.
 (ii) Iron does not occur commonly in higher oxidation states.
 (iii) Scrap iron is added in the manufacture of ferrous sulphate heptahydrate from iron pyrites.
- 15.11 Comment on the followings
 (a) Almost all the transitional elements utilize orbitals in forming compounds but zinc, cadmium and mercury do not utilize.
 (b) Zinc is more reactive than magnesium.
 (c) Copper (+2) forms stable compounds but CuI_2 is not obtained.
 (d) Among transition elements, the first element in a group normally differs from other elements but in zinc group both zinc and cadmium are very closely related.
- 15.12 Mention some of the important uses of iron, copper, mercury and zinc and their compounds.
- 15.13 Give preparation, properties and uses of the followings: (i) silver nitrate, (ii) ferric chloride, (iii) copper sulphate, (iv) Mohr's salt, and (v) Calomel.
- 15.14 Define with explanation each of the following terms:
 (a) stainless steel (b) alloy steels (c) double salt and (d) refractory metals or compounds

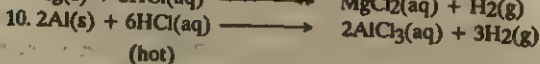
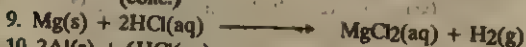
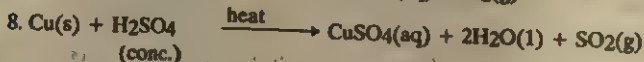
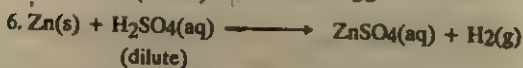
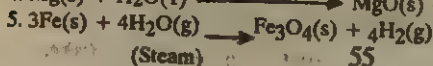
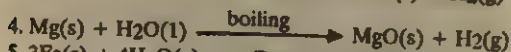
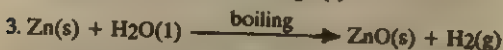
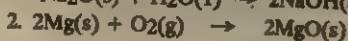
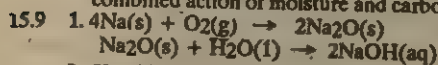
- 15.15 Give the approximate composition and properties of :
 (i) pig iron, (ii) cast iron, (iii) wrought iron and, (iv) steel.
- 15.16 Discuss the merits and demerits of using oxygen in place of hot air in the Bessemer converter and blast furnace.
- 15.17 (a) Name with their composition five alloy steels and five alloys of copper and silver. Mention some of their possible uses.
 (b) Mention some of the reasons for the wide use of iron and steel.
- 15.18 Give the composition, the formulac and uses of the following:
 (a) Bordeaux mixture, (b) Blue vitriol (c) Paris green (d) Verdigris, (e) Lunar caustic (f) Green vitriol and (g) Alnico.
- 15.19 (a) Suggest a method of preparing copper sulphate from copper turnings and silver nitrate from an alloy of silver and copper.
 (b) Describe the action of heat on:
 (i) copper sulphate (ii) ferrous sulphate (iii) silver nitrate
- 15.20 Give the brief methods adopted in the metallurgy of iron, copper, silver and lead.

ANSWERS TO SELF ASSESSMENT QUESTIONS

- 15.1 (i) a, (ii) a, (iii) b, (iv) c, (v) c, (vi) a, (vii) a, (viii) a, (ix) c, (x) d, (xi) c, (xii) d, (xiii) b, (xiv) b, (xv) a.
- 15.2 (i) amphoteric (ii) metallurgy (iii) gangue or matrix, (iv) hydraulic washing (v) calcination (vi) ore is heated in presence of air (vii) tempering (viii) cathode (ix) galvanizing (x) froth flotation
- 15.3 (i) T, (ii) T, (iii) T, (iv) F, (v) F, (vi) F, (vii) T, (viii) F, (ix) F, (x) T, (xi) T, (xii) T, (xiii) T.
- 15.4 1. (viii) 2. (i) 3. (iii) 4. (xi) 5. (vi) 6. (v) 7. (iv) 8. (vii) 9. (ix) 10. (ii) 11. (x)
- 5.5 1. When aqueous ammonia is added to a solution of copper sulphate, bluish white ppt. of $\text{Cu}(\text{OH})_2$ is formed which dissolves on adding excess of aqueous ammonia solution forming copper ammonia complex having deep blue colouration: $[\text{Cu}(\text{NH}_3)_4]^{2+}$
2. HNO_3 gets reduced to NO_2 and Sn is oxidized to H_2SnO_3
3. PbO_2 and $\text{Pb}(\text{NO}_3)_2$ are formed
- 15.6 1. The actual reducing agent of haematite in blast furnace is CO
2. Galena ore (PbS) is roasted at moderate temperature in excess of air on the hearth of reverberatory furnace. The ore is oxidized partly to oxide and partly to sulphate..
3. Zinc is a stronger reducing agent than copper and is also cheaper. This is why Zn and not Cu is used for the recovery of metallic Ag from complex $[\text{Ag}(\text{CN})_2]^-$
 $2[\text{Ag}(\text{CN})_2]^- + \text{Zn} \rightarrow 2\text{Ag} + [\text{Zn}(\text{CN})_4]^{2-}$
4. Chalcocite Cu_2S is roasted and not calcined because free supply of air is required to convert to its oxide.
 $2\text{Cu}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$
1. $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \rightarrow 6\text{Cu} + \text{SO}_2$
 In calcination, heating is done in the absence of air.
- 15.7 1. Copper pyrites : Sulphide ore is crushed, concentrated and then roasted. The roasted ore is then smelted in the blast furnace. In smelting, the roasted ore, i.e., oxide is reduced to metal.
2. Zinc blende : Sulphide ore is crushed, concentrated and then roasted. During roasting a small amount of zinc sulphate is also formed along with oxide. The oxide is reduced with powdered coal in fire clay retorts (smelting).
3. Haematite : Purified oxide is put to smelting in the blast furnace.
- (ii) See the text
- (iii) $\text{Ag} + 2\text{H}_2\text{SO}_4 \longrightarrow \text{Ag}_2\text{SO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$
 $2\text{Ag} + 4\text{HNO}_3 \longrightarrow 2\text{AgNO}_3 + 2\text{NO}_2 + 2\text{H}_2\text{O}$



(ii) A green deposit of basic copper carbonate is formed. It is because of the combined action of moisture and carbon dioxide present in air.



Structure and Shapes of Hydrocarbons

One of the most striking evidences of the reliability of the chemist's methods of determining molecular structure is the fact that he has never been able to derive satisfactory structures for supposed molecules which are in fact nonexistent.

LOUIS P. HAMMETT

UNIT PREVIEW

16.1 Introduction

16.2 Alkanes

16.3 Conformation in hydrocarbons

16.4 Isomerism

16.4.1 Structural isomerism

16.4.2 Stereoisomerism : (a) geometrical isomerism and (b) optical isomerism

16.5 Enantiomers - origin of chirality

16.5.1 Optical rotation

16.6 Alkenes

16.7 Alkynes

16.8 Arenes

16.8.1 Structure of benzene

16.8.2 Resonance

16.8.3 Isomerism in arenes

Self assessment questions

Terminal questions

Answers to self assessment questions

LEARNING OBJECTIVES

At the completion of this unit, you should be able to:

1. Classify the hydrocarbons into (i) alkanes, (ii) alkenes, (iii) alkynes, and (iv) arenes.
2. Explain the difference between aliphatic and aromatic hydrocarbons.
3. Describe the structural features of different types of hydrocarbons
4. Understand the meaning of isomerism.
5. Describe the different types of isomerism like structural isomerism, conformational isomerism and stereoisomerism.

16.1 INTRODUCTION

There is such a vast number of organic compounds that we can only hope to skim this area of study. As beginners, it is wise to note from the onset that organic chemistry is systematically organized into the study of groups of substances. Each group of compounds have some common features of their molecular structures. With the help of chemical reactions shown by certain representative compounds in each of these group, we learn the chemistry of many related substances.

The simplest organic compounds are hydrocarbons, containing carbon and hydrogen only. They occur mainly in coal, natural gas and petroleum. These naturally occurring hydrocarbons provide the starting material for the preparation of the bulk of the world's synthetic organic compounds. Thus, they can be considered as the derivatives of hydrocarbons obtained by substituting hydrogen with an appropriate functional group (Unit 7). Hydrocarbons are described as either aliphatic or aromatic (Fig. 16.1). Aliphatic compounds, based upon their structure and chemical reactivity, hydrocarbons can be grouped into three classes: (i) alkanes, (ii) alkenes, and (iii) alkynes, (which exist both

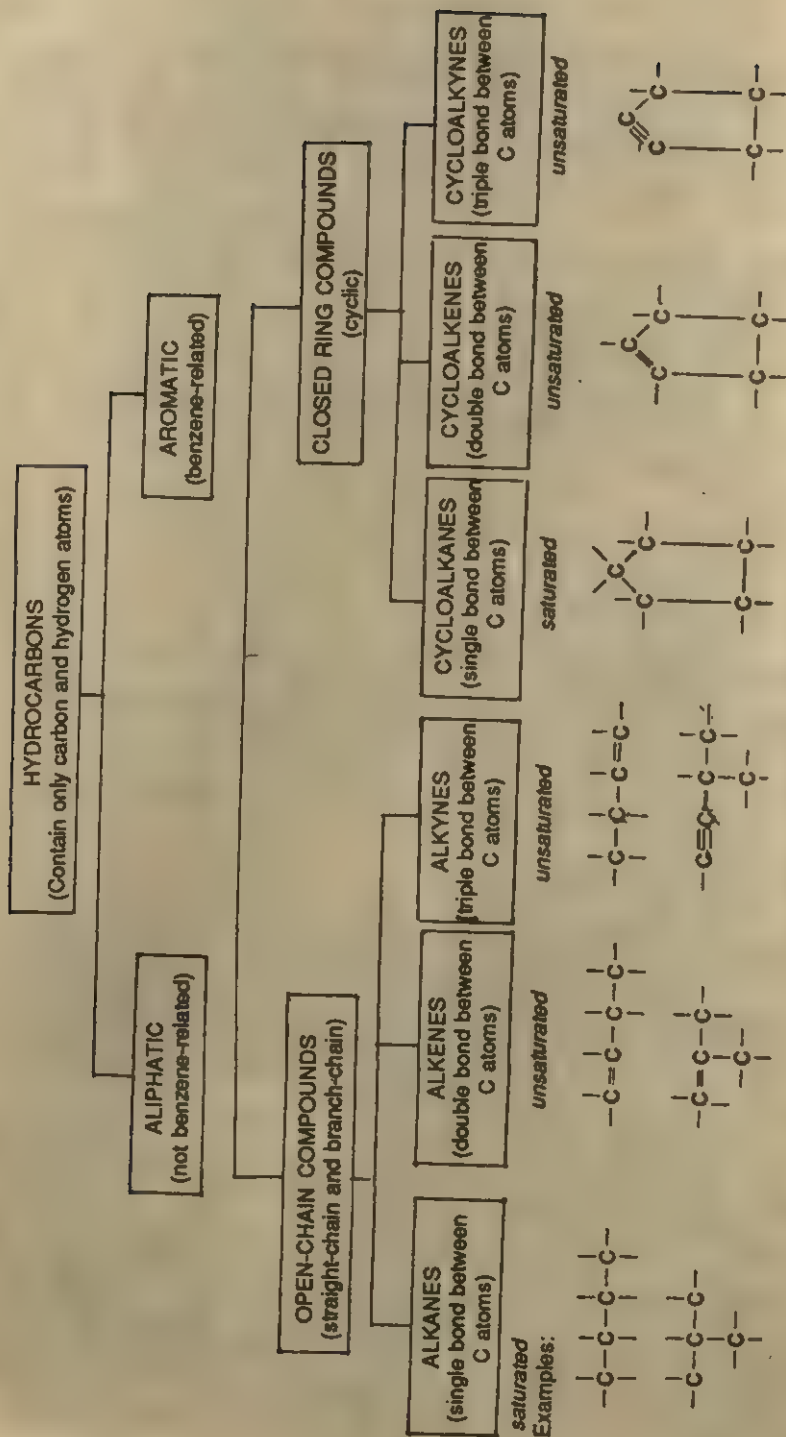


Fig. 16.1 Families of hydrocarbons

as open chains, — acyclic and rings -cyclic molecules). Aromatic compounds have conjugated ring systems. Alkanes are saturated hydrocarbons with only carbon - carbon single bonds. Alkenes and alkynes are unsaturated hydrocarbons with at least one carbon – carbon double and triple bond respectively.

16.2 ALKANES

Alkanes are ~~saturated~~ hydrocarbons which are also known as paraffins (para=less; affins=affinity). In these compounds, the tetra-covalent nature of carbon is established by single bonds to carbon and hydrogen atoms. The general formula of alkanes is C_nH_{2n+2} . Cyclo-alkanes can be represented by the general formula C_nH_{2n} (for monocyclic) or C_nH_{2n-2} (for bicyclic) and so on. The formation of only single bonds requires that each carbon atom in an alkane be sp^3 hybridized and the four bonds that it forms are directed towards the four corners of a tetrahedron. In methane, the simplest alkane, the four hydrogen atoms surrounding the carbon atom are arranged at the corners of a regular tetrahedron (Fig. 16.2a). A tetrahedron is a regular geometric figure with four faces and six edges. The angles between each pair of bonds in a tetrahedral molecule are $109^\circ 28'$. Each face of the tetrahedron is an equilateral triangle and has three hydrogen atoms.

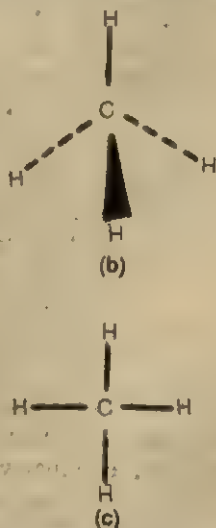
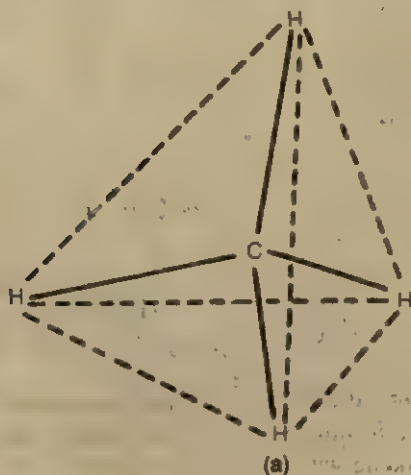
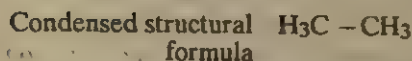
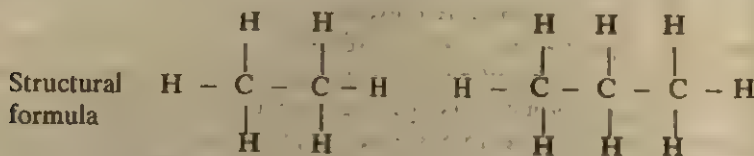


Fig. 16.2 (a) : Three dimensional arrangement of methane.

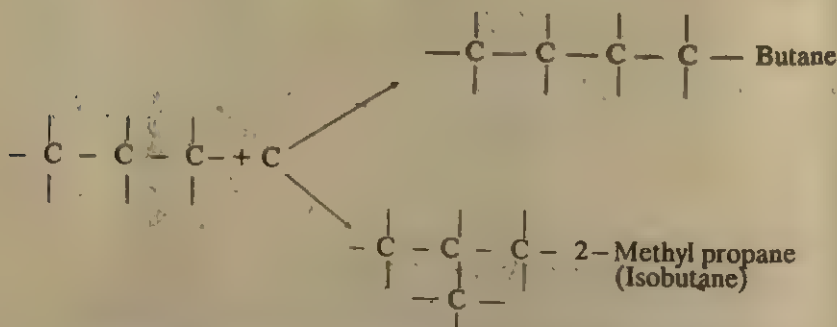
Fig. 16.2 (b) & (c) Spatial formula of methane.

Le Bel and Van't Hoff in 1873 showed that methane molecule is three dimensional. Figures 16.2 (b) or 16.2 (c) portray the usual way of representing methane. The dark thick line in Fig. 16.2 (b) indicates a C – H bond projecting towards the reader and the regular line, indicates a

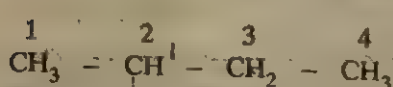
C-H bonds in plane of the page and the two dotted lines indicated C-H bonds projecting behind the plane of the page. Figure 16.2 (c) is a two dimensional structural formula. It does not portray the actual tetrahedral shape of the methane. Ethane and propane are illustrated below through their structural formulae and condensed structural formulae.



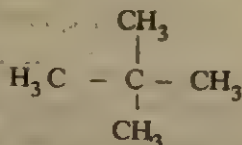
Through the above representations, we are not specifying the geometry of ethane and propane. There is free movement along the carbon backbone. On the other hand, beginning with butane, it is possible to describe the molecular structure of an alkane in ways that lead to different compounds. This is because, the fourth carbon can be placed in the skeleton either at the two ending carbons or at the middle carbon atom.



These two compounds with different structural arrangements of their atoms but same molecular formulae (C_4H_{10}) are called *structural isomers*. In a similar way, an alkane with molecular formula C_5H_{12} will have three structural isomers.



2-Methylbutane



2,2-Dimethylpropane

With increase in the number of carbon atoms the number of structural isomers possible for a given molecular formula also increases, e.g., $C_{10}H_{22}$ shows 75 structurally isomeric forms. The carbon atoms in a compound are designated according to the number of carbons to which they are directly attached (Unit 7). A carbon atom bonded to only one other carbon or to none is called a primary carbon (denoted by 1°). Similarly, a secondary carbon (2°) is bonded to two carbons, a tertiary (3°) to three and a quaternary (4°) to four.

16.3 CONFORMATION IN HYDROCARBONS

Although, we know that the four bonds around each carbon atom in ethane are arranged on the four corners of a tetrahedron, this does not tell us how the C-H bonds at one end of the molecule are oriented with respect to those at the other end. Because of the possibility of free movement along the carbon backbone, it is possible to rotate one CH_3 group of ethane about the carbon-carbon bond keeping the other fixed without affecting the σ bond. This rotation gives rise to different conformations of the molecule. Two different arrangements of atoms (conformations) in a molecule are shown in Fig 16.3 drawn end on (Newman projection) and on an angle (Saw horse projection). In one form of the molecule, the C-H bonds at one end of the molecule are directly opposite the C-H bonds at the other end. The C-H bonds are said to have eclipsed arrangement. In the other form, the C-H bonds at one end of the molecule, rather than being exactly opposite the bonds at

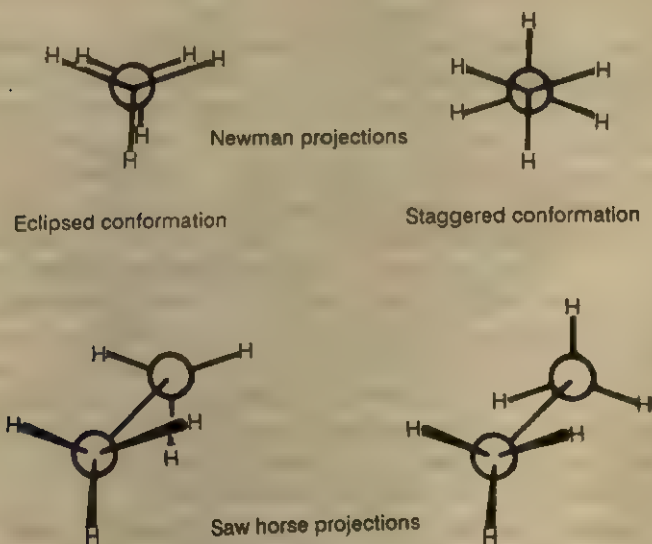


Fig. 16.3. Rotational conformations of ethane.

the other end, lie exactly between them. The C – H bonds are said to have a **staggered arrangement**. In between these two conformations, infinite number of conformations corresponding to intermediate positions of hydrogen are said to be **skew conformations**. The hydrogen atoms on adjacent carbon atoms are quite close to each other in the eclipsed conformation, in which the potential energy of the system is at a maximum. The staggered conformation corresponds to a minimum of potential energy (Fig. 16.4). It means that the eclipsed conformation

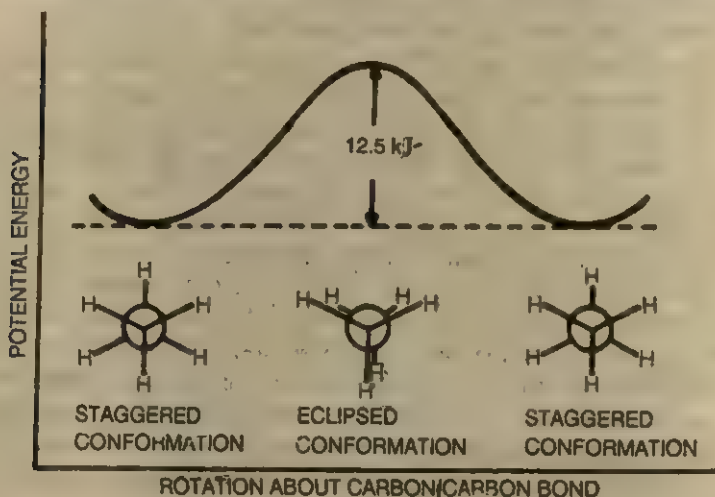


Fig. 16.4. Variation of the potential energy of ethane with rotation about the carbon – carbon bond.

with a slightly higher energy is less stable than staggered conformation. The energy difference between the two conformations is only 12.5 kJ mol^{-1} which at room temperature is too small a barrier to prevent free rotation about the carbon–carbon bond. In effect, one end of the molecule is continually rotating with respect to the other end. The free rotation is easily demonstrated by using a ball-and-stick model of ethane (Fig. 16.5). However, the combined effect of many such barriers influences the shape of a large aliphatic or alicyclic molecule. Propane is written $\text{CH}_3 - \text{CH}_2 - \text{CH}_3$ and is designated as a straight chain hydrocarbon. This is somewhat misleading, since with tetrahedral bond angles the carbon chain is bent as shown in Fig. 16.6. Further, the barrier to rotation about a carbon–carbon bond is expected to be slightly higher for propane than for ethane, because a methyl group is a bulkier than a hydrogen atom. The eclipsed conformation of propane is higher in energy by 13.8 kJ mol^{-1} than the staggered conformation.

Conformational isomerism is possible in alicyclic compounds as well. Alicyclic compounds, a subgroup of the alkanes are the cyclic compounds in which the carbon chain is joined together to form a cyclic structure.

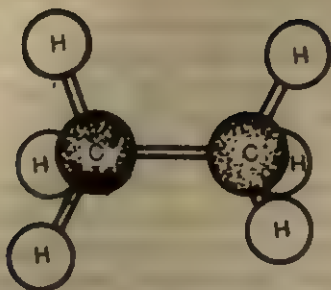


Fig. 16.5. 'A ball and a stick model of ethane molecule.

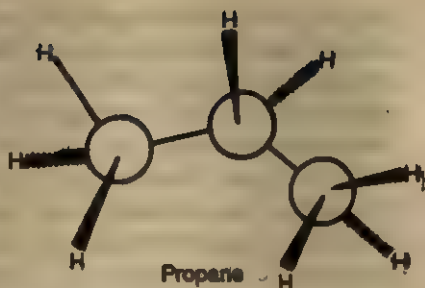
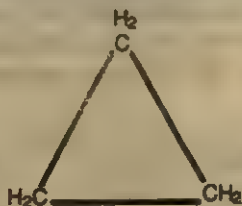
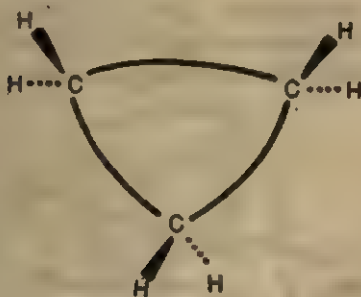
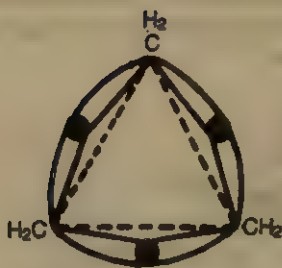


Fig. 16.6 Three dimensional representation of propane.

Cyclic carbon rings result in a distortion of the bond angle causing considerable intermolecular strain and steric hindrance to free rotation. The simplest cyclic compounds is cyclopropane, in which the bond angle, $C - C - C$ is distorted to 60° (Fig. 16.7a). This is rather large deviation



(a) OLD PICTURE



(b) 'BENT BONDS' IN CYCLOPROPANE



Fig. 16.7 Structure of cyclopropane

from the most stable tetrahedral angle of $109^\circ 28'$. But in the modern representation of cyclopropane, though the internuclear angle is 60° , the orbital angle is about 104° . It means that the region of maximum orbital overlap does not correspond to the internuclear axis and the carbon-carbon bonds are described as bend-bonds (Fig. 16.7 b). The bonds are bent, however, so that overlap between orbitals is not only reduced, but also strained in the same way that any steel spring would be distorted. The cyclopropane molecule suffers still another kind of strain. Figure 16.7c shows that $-C-H$ bonds are all eclipsed, and therefore, somewhat strained because of the mutual repulsion of electron pair on carbon atoms. Thus, the cyclopropane is unstable and undergoes ring opening reactions with many reagents. Generally, the cyclic compounds whose bond angles differ significantly from $109^\circ 28'$ are unstable and have high energy.

As rings increase in size, bond angles increase and strain is less. Thus, in conformity with the geometric requirement for the tetrahedral carbon atom, higher ring structures are puckered or non-planar. Cyclopentane is such a system, in which the bond angle (108°) is close to the tetrahedral angle of $109^\circ 28'$ and is, therefore, quite stable and unreactive.



Cyclohexane, C_6H_{12} is a puckered molecule and adopts chair or boat conformations (Fig. 16.8). Of the two, the chair form is more stable, the energy difference being about 44 kJ mol^{-1} .

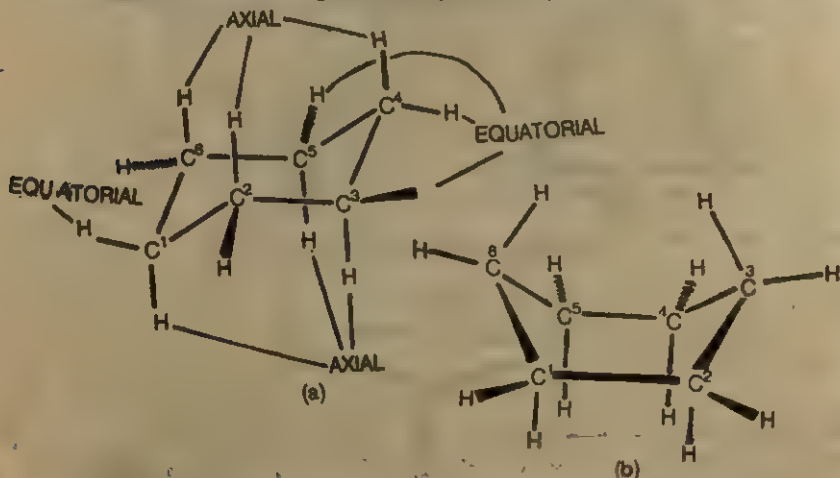


Fig. 16.8 (a) Chair, and (b) boat conformations of cyclohexane.

This is because in the boat form, many hydrogens on adjacent carbon atoms correspond to the unfavourable eclipsed conformations of ethane (Fig. 16.9). Also the two hydrogen atoms attached to C_3 and C_6 are quite close to repel one another. On the other hand, in the chair form we observe the staggered arrangement of groups (as in ethane) and an interaction between C_1 , C_2 , C_3 and C_4 similar to that in gauche butane (Fig. 16.10).

16.4 ISOMERISM

Isomers are compounds that have an identical molecular formula, but have a different arrangement of atoms within the molecules and the phenomenon is called isomerism. Isomers can be readily distinguished from each other because of differences in physical or chemical properties. There are two main types of isomerism:

1. Structural isomerism.
2. Stereoisomerism

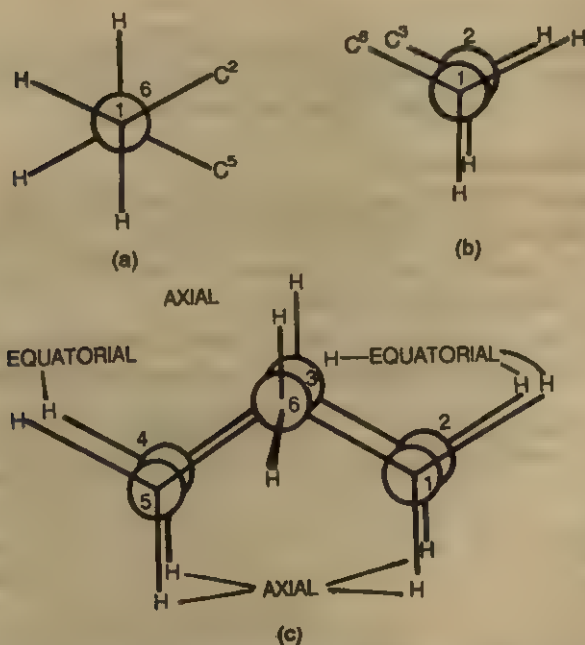


Fig. 16.9 (a) Cyclohexane in boat conformation (a) viewed down the C_1, C_6 bond, and (b) viewed down C_1 and C_2 bond (c) Projection of cyclohexane in boat conformation.

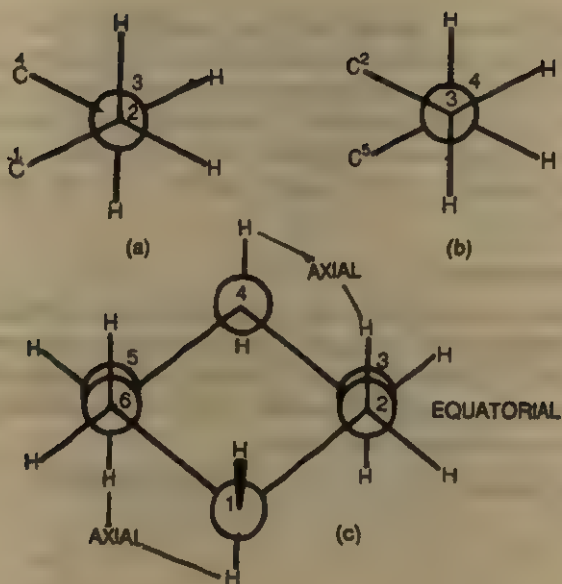


Fig. 16.10 Cyclohexane in chair conformation (a) viewed down the C₂, C₃ bond, and (b) viewed down the C₃ and C₄ bond. (c) Projection of the cyclohexane in the chair conformation.

16.4.1 Structural Isomerism

Structural isomers are compounds in which the atoms in the molecule are linked in different ways, i.e., there are 'gross' differences between the structures of the isomers. Structural isomers may be subdivided under the following groups:

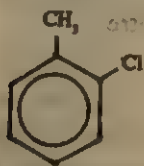
(a) **Chain Isomerism** : Isomers in which different carbon skeletons are said to display chain isomerism, e.g., the two isomers of butane :

Structural isomers of C ₄ H ₁₀	Carbon skeleton	Name
CH ₃ - CH ₂ - CH ₂ - CH ₃	C - C - C - C	Butane
CH ₃ - CH - CH ₃ CH ₃	C - C - C C	2-Methyl-propane

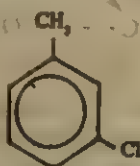
(b) **Position Isomerism** : Isomers in which the carbon skeleton is identical, but the location of substituent groups is different are said to display position isomerism, e.g., the two isomers of monochloropropane:

Position isomers of C_3H_7Cl	Skeleton	Name
$CH_3 - CH_2 - CH_2 - Cl$	$C - C - C - Cl$	n-Propylchloride
$CH_3 - CH - CH_3$ $\quad \quad \quad $ $\quad Cl \quad \quad Cl$	$C - C - C$ $\quad \quad \quad $ $\quad Cl \quad \quad Cl$	Isopropylchloride

Among disubstituted aromatic compounds three structural isomers are possible.



o-Chlorotoluene

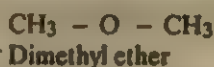


m-Chlorotoluene

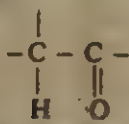


p-Chlorotoluene

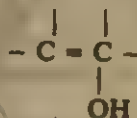
(c) **Functional Group isomerism** : Isomers which have different functional groups (i.e., belong to different families) are said to display functional group isomerism, e.g., an alcohol and an ether :



(d) **Tautomerism** : Isomers which exist in dynamic equilibrium between themselves are said to display tautomerism. Tautomers are usually not equally stable :



Keto-tautomer

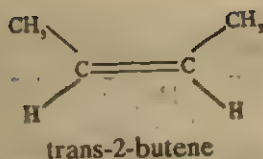
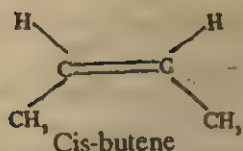


Enol-tautomer

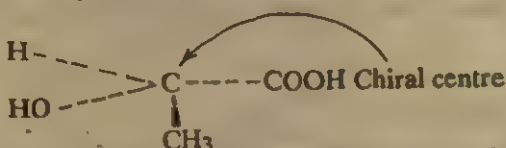
16.4.2 Stereoisomerism

Isomers in which some atoms or groups are present in different arrangements in space are said to display stereoisomerism (stereo means 'space' in Greek). That is, stereoisomers differ in their three dimensional structures. Stereoisomerism is of two types:

(a) **Geometrical Isomerism** : Due to rigidity (restricted rotation) of double bonds, 2-butene can exist in two isomers. These two isomers differ in that the two methyl groups (or the two hydrogen atoms) are attached to the doubly bonded carbon atoms either on the same side of the plane of the double bond or on opposite sides.



(b) Optical Isomerism (origin of chirality) : Isomers that are capable of rotating the plane of plane-polarized light are said to display optical isomerism. A carbon atom attached to four different atoms or groups is called an asymmetric carbon atom and is said to possess a 'chiral centre'.



Le Bel and van't Hoff in 1873 suggested that the four bonds of carbon are directed to the corners of a tetrahedron (Fig. 16.11). Thus, tetrahedral models of a molecule, Cabde, containing a chiral centre, can be built in two ways such that they are related to each other as an object to its mirror image (Fig.16.12). However, the object and the mirror image, i.e., the two models are *non-superimposable*. Such a molecule which is non-superimposable on its mirror image is called a 'chiral molecule' or an 'asymmetric molecule or a dissymmetric molecule'. Objects that possess neither a plane * (σ) nor a centre(i) of symmetry**

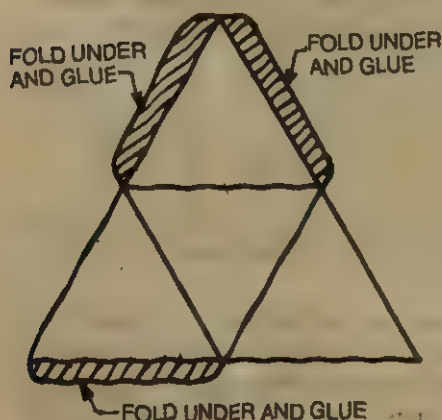


Fig. 16.11. Making a card board tetrahedron

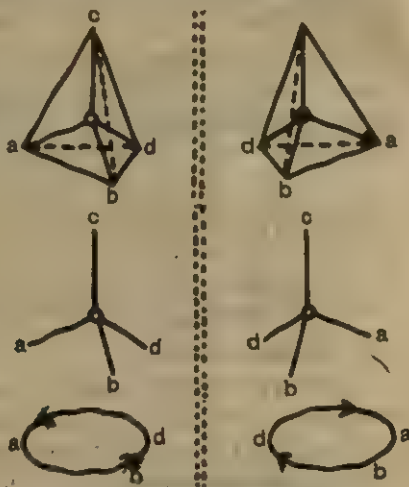


Fig. 16.12. Mirror image of an asymmetric compound Cabde

* The plane of symmetry (σ) is defined in terms of the reflection operation. Thus, for every point on the object a corresponding point is found by moving from the original point in a line perpendicular to the plane to an equal distance on the other side of the plane.

** The centre of symmetry (i) is a point in the object through which is applied the inversion operation. In this operation an imaginary line is drawn from any point on the object through the centre (i) and extended beyond it for an equal distance. Inversion means that this latter point will correspond to the original point.

(Fig. 16.13) are also called chiral objects. These objects are capable of existing in right handed and left handed forms. Some common examples of objects which are not super-imposable on their mirror images are, the letter B, C, D, E, F, G, J, K, L, N, P, Q, R, S, Z. The left and the right hands are mirror images of each other but are non-superimposable (Fig. 16.14). Other objects typical of this group are ears, feet, screws, propellers, coils, etc.

Objects that possess either a plane (σ) or a centre (i) of symmetry or both are superimposable on their mirror images and are said to be achiral. Examples are hammers, coffee cups, ice- cream cones, barrels, balls, simple chairs, button and tables (Fig. 16.15). Alphabets, A, H, I, M, O, T, U, V, W and X also belong to this class of objects. The importance of molecular chirality will be clarified in the discussion.

16.5 ENANTIOMERS (ORIGIN OF CHIRALITY)

If two or three groups attached to a tetrahedral atom are the same (Fig. 16.16b) the molecules are superimposable on their mirror images and no isomers exist. A tetrahedral atom that has four different groups attached (Fig. 16.16a) cannot be superimposed on its mirror image and the two mirror image structures are isomers, called enantiomers. All objects, including molecules, have mirror images. For some object, there is a difference between the object and its reflection. It is only an asymmetric object—an object we can describe as right-handed or left handed—that differs from its reflection.

This characteristic of being either right or left handed is called chirality and molecules possessing it are chiral (from the Greek word: cheir, handedness). All optically active molecules are chiral and one enantiomer is right handed, the other left handed.

They show different effect on light when they interact with the plane polarized light - radiation whose electromagnetic waves all lie in the same plane.

Thus, enantiomers are stereoisomers which are non-superimposable mirror images. They have the following important characteristics.

(i) They have identical physical properties except optical rotation. Their melting points, boiling points, solubilities in different solvents, etc., are all identical. Because of this identity, attempts on their separation by usual chemical methods, like distillation, fractional distillation, crystallization, etc., are futile. They rotate the plane of polarized light equally but in opposite directions. The isomer which rotates the plane of polarization to the right is said to be dextrorotatory and the value is given a (+) sign. The enantiomer which rotates the plane of polarization to the

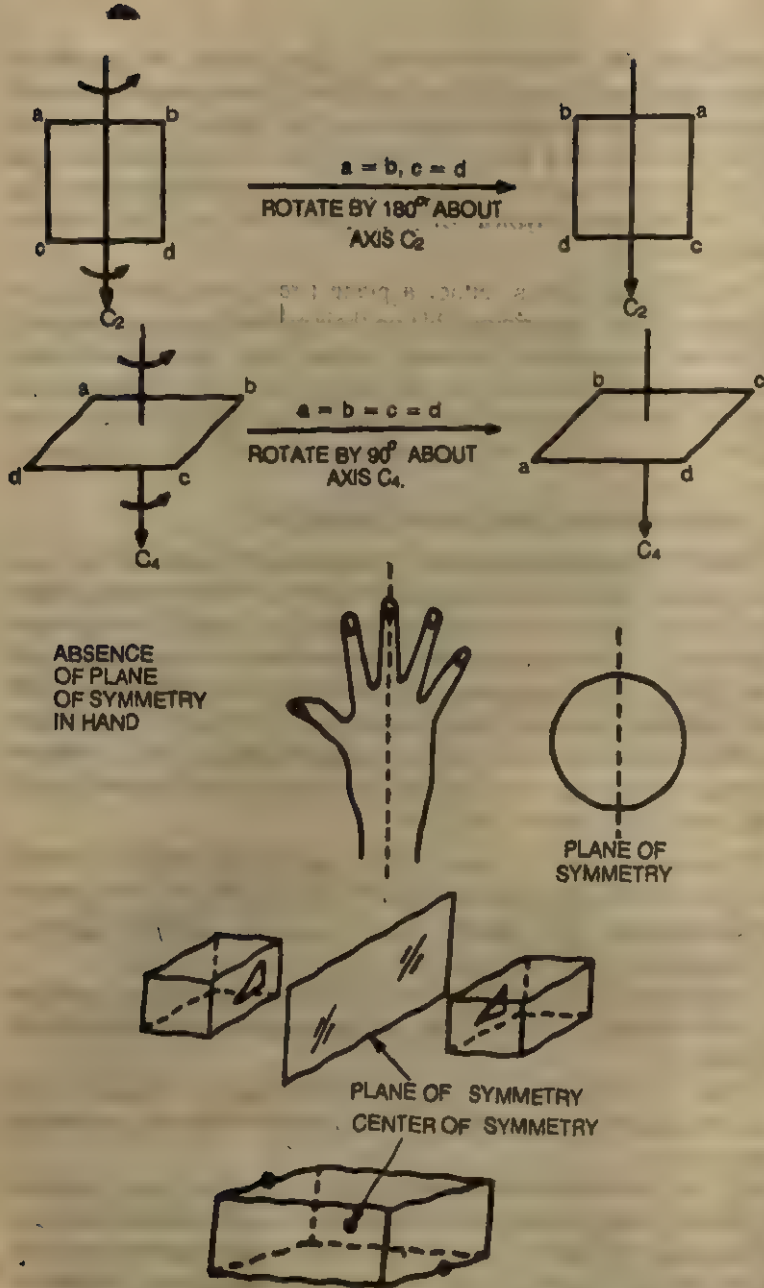


Fig. 16.13. Examples of symmetry element and symmetry operations.

left is said to be laevorotatory and is given a $(-)$ sign.

(ii) They have identical chemical properties except in reactions

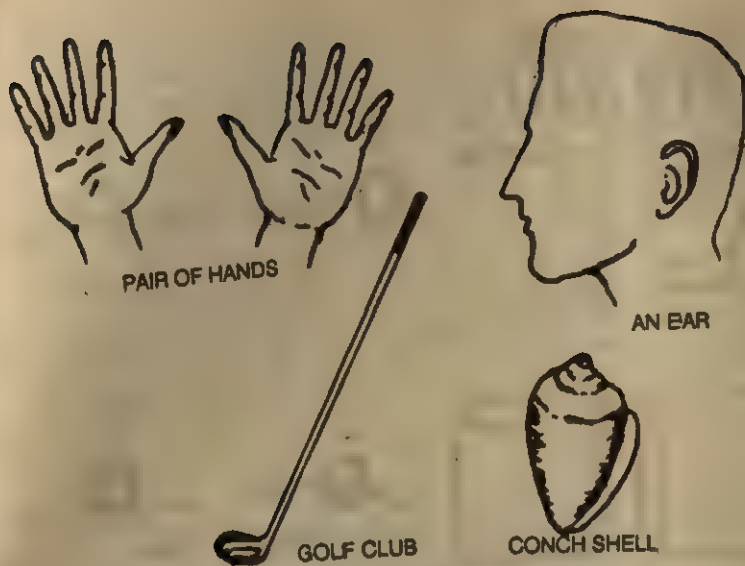
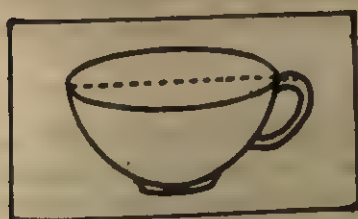
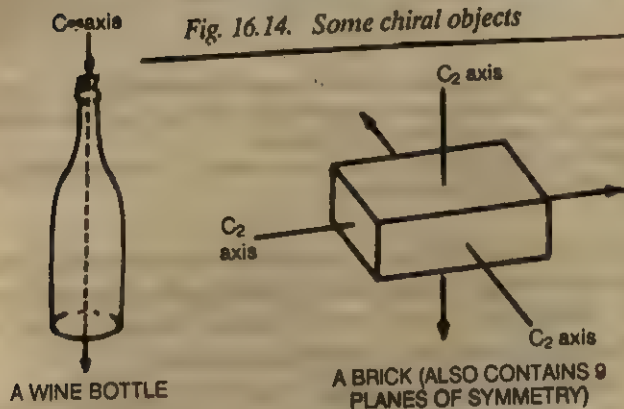


Fig. 16.14. Some chiral objects



COFFEE CUP
(A PLANE OF SYMMETRY
CUTS THE CUP AND HANDLE)

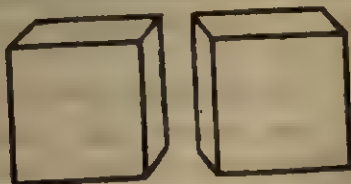
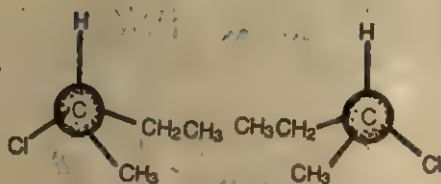
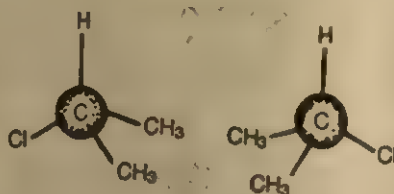


Fig. 16.15 Some achiral objects.

with other chiral molecules. Ordinary chemical reactions of enantiomers are not only identical in nature but the rates of reaction are also identical.



(a)



(b)

Fig. 16.16 (a) Non-superimposable mirror images (enantiomers). A pair of hands and a pair of 2-chlorobutane molecules are examples of enantiomers. In these examples, the plane of symmetry is absent.

(b) Superimposable image: A cube and a molecule of 2-chloropropane are each symmetric. They are not enantiomers.

(iii) They often have differences in bio-chemical properties. Thus, one enantiomer of the drug, amphetamine is much more effective than its mirror image. Similarly (+) and tartaric acid is metabolized by the mould penicillium glaucum while (–) tartaric acid is not.

(iv) A mixture of equal quantities of the (+) and (–) forms is optically inactive and is called a **racemic mixture** and is designated by the sign (\pm). The process of separation of racemic mixture is called '**resolution**'.

16.5.1 Optical Activity (optical rotation)

Plane polarized light : Light is propagated by wave motion. In ordinary light the vibrations of waves occur in all planes at right angles to the lines of propagation. However, if such a beam of light is passed through a Nicol prism, the resulting beam has waves vibrating in the same plane, vibrations in other places being cut off. Light, whose vibrations occur in a single plane only, is known as **plane polarized light** and the phenomenon is known as **polarization**. When plane polarized light is passed through solutions of certain organic compounds, its plane of polarization is rotated by a certain angle either towards left or right. The

phenomenon of rotating the plane polarized light is called **optical activity** and the substances which rotate plane polarized light are known as **optically active**. Solutions of compounds like lactic acid, glucose, 2-chlorobutane rotate plane polarized light. Hence, these compounds are optically active. Those substances which rotate the plane polarized light to right are called dextrorotatory represented by sign 'd' or (+) and those which rotate to the left are called laevorotatory represented by sign 'l' or (-).

Nicol prism (Fig. 16.17) is named after William Nicol in 1828, who used it for the first time. It is made of an iceland spar crystal (calcite or crystalline CaCO_3). The crystal is cut diagonally and joined again with the help of canada-balsam.

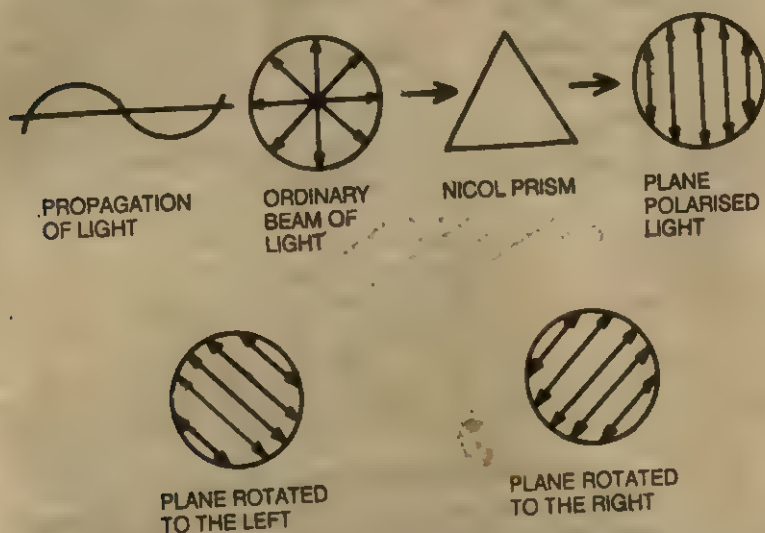
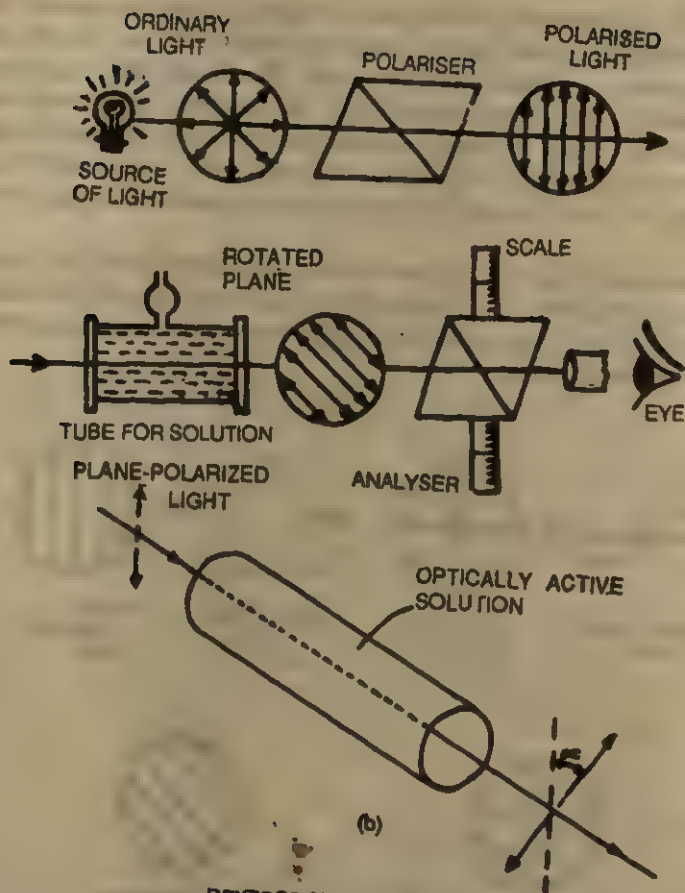


Fig 16.17 Imaginary cross-section of light beams.

Measurement of optical rotation : The instrument used for measuring optical rotation of a plane polarized light is called polarimeter (Fig. 16.18). A polarimeter consists of a polarizer and an analyzer with a solution tube between them. The solution under examination is kept in this tube. The analyzer is fitted with a rotating scale to note the angle through which the analyzer is rotated in an experiment. The readings are taken with the help of an eye-piece fixed next to analyzer.

The magnitude of rotation depends upon the following factors:

- (i) Nature of the substance
- (ii) Concentration of the solution
- (iii) Wavelength of the light used
- (iv) Nature of the solvent



DEXTROROTATORY OPTICAL ACTIVITY.

Fig. 16.18. (a) Schematic representation of a polarimeter, (b) The plane polarized light, passes through a solution; the light is rotated through an angle either to the right (dextro) or the left (laevo).

- (v) Temperature of the solution
- (vi) Thickness of the layer traversed by polarized light.

The rotatory power of a given solution is usually expressed as specific rotation $[\alpha]$.

$$\text{Specific rotation } [\alpha]_{\lambda}^t = \frac{\alpha_{\text{obs.}}}{l \times c}$$

Where

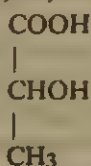
- α_{obs} = observed rotation
- l = length of the solution in decimetre
- c = g of substance in 1 mL of solution
- t = temperature
- λ = wavelength

Specific rotation is defined as the observed angle of rotation when plane polarized light passes through a solution of 1 decimetre length and 1 g per cm^3 concentration.

Optical isomers of lactic acid : Lactic acid is representative example of molecules containing 'chiral centre'. We have already seen the tetrahedral representation of an optically active molecule, Cabde. But it is much more convenient to study optical isomers (those having an open chain structure) with the help of Fischer projection formulae.

The rules governing the representation by Fischer projection are best understood with the help of an example, i.e., (+) lactic acid.

(i) The carbon chain is written vertically, keeping the highest oxidized carbon at the top, i.e.,

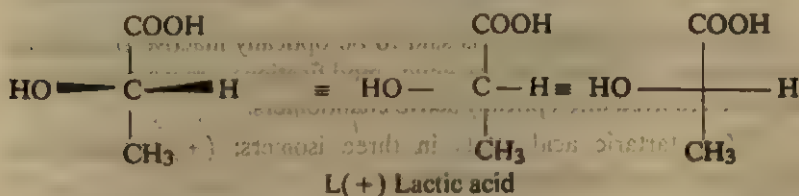


(ii) The functional groups are represented either to the left or right.

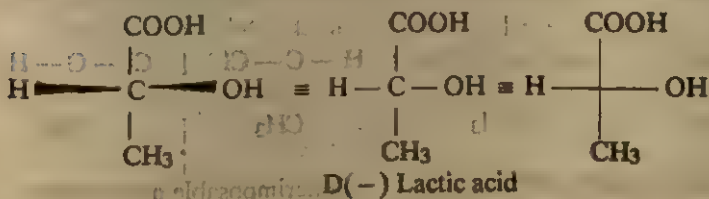
(iii) The groups at the top and bottom of the projection formula represent groups in the asymmetric molecule which are behind the plane of projection. The plane of projection is passing through the asymmetric carbon atom.

(iv) The groups at the left and right in the projection formula represent groups in the asymmetric molecule which are above the plane of projection.

Thus, dextrorotatory lactic acid is represented as:



Similarly, the laevorotatory lactic acid would be represented as

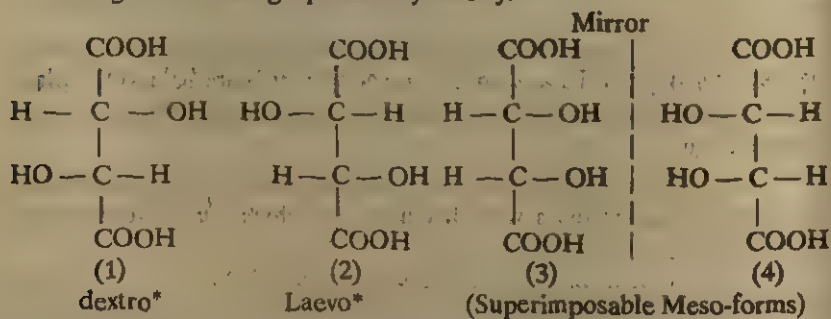


By a convention, in a Fischer projection formulae, if the first functional group, from the bottom to the right is called a D-isomer. Thus, the laevorotatory lactic acid is to be designated as D(-) lactic acid. And, if the first functional group from the bottom is to the left, then it is designated as a L-isomer. Thus, dextrorotatory lactic acid is designated as L(+) lactic acid.

The term 'configuration' means the arrangement in space of atoms or groups around a chiral centre. Thus, the two projection formulae above represent the two configurations of lactic acid.

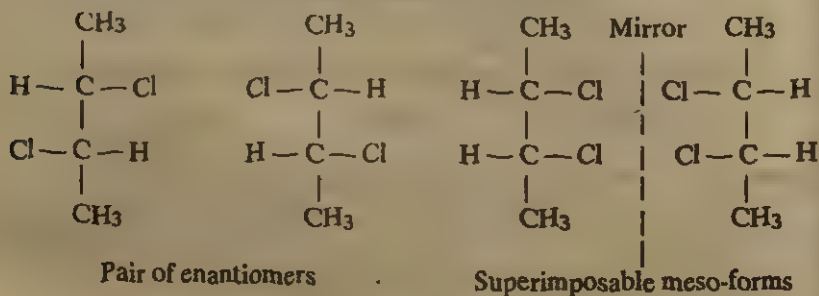
Molecules with two chiral centres : Tartaric acid is a well known example of molecules with two chiral centres. Though, we can write down four projection formulae for tartaric acid, two of these are identical and represent the same molecule.

Structures (3) and (4) are superimposable mirror images and are thus, identical and optically inactive. Thus, configuration (3) or (4), inspite of having two chiral centres is itself a non-chiral configuration. They have a plane of symmetry which is indicated in the formulae with a dotted line. These stereoisomers are called the **meso-form**. A meso-form is a configuration having a plane of symmetry.



The meso-configuration is said to be optically inactive by internal compensation. Unlike the racemic modifications, meso-compounds cannot be resolved into optically active enantiomers.

Thus, tartaric acid exists in three isomers: (+)-tartaric acid, (-)-tartaric acid and meso-tartaric acid.



2,3-Dichlorobutane, is another molecule which has two chiral centres and, therefore, can exist in three forms (+) form, (-) form and the meso-form.

16.6 ALKENES

The alkenes (C_nH_{2n}), a group of hydrocarbons with two fewer hydrogen atoms than the alkanes, are unsaturated hydrocarbons in that they can add two hydrogens to become alkanes. These molecules are characterized by the presence of a π bond between two adjacent carbon atoms. The simplest parent member of the alkene series is ethene (ethylene), C_2H_4 . An older name of alkenes, still in use, is olefins meaning oil forming.

Members of the alkene family with their condensed structural formulae are listed in Table 16.1. They all have one double bond between two carbon atoms. All the names of the alkenes end in 'ene'.

TABLE 16.1 Simple alkenes

Molecular formula	Name	Condensed structural formula
C_2H_4	Ethene (ethylene)	$CH_2 = CH_2$
C_3H_6	Propene (propylene)	$CH_2 = CHCH_3$
C_4H_8	Butene (butylene)	$CH_2 = CHCH_2CH_3^*$
C_5H_{10}	Pentene	$CH_2 = CHCH_2CH_2CH_3$
C_6H_{12}	Hexene	$CH_2 = CHCH_2CH_2CH_2CH_3^*$

* One of the possible isomers

In ethene, the carbon atoms are bonded to each other and to the two hydrogen atoms by three equivalent sp^2 hybrid orbitals, which form a planar arrangement of σ bonds with bond angles of 120° . The unhybridized p-orbital on each carbon atom is occupied by a single electron. The p-orbitals on each carbon overlap as illustrated through Fig. 16.19 to form a π bond by overlap of the lobes both above and below the plane of the molecule. Therefore, the π bond between the two carbon atoms is perpendicular to this plane. Thus, the double bond is formed by superposition of a sigma and a p π bond. A σ bond has a symmetry axis along the C-C bond, but a π bond lacks this symmetry. However, the π bond is bisected by the plane containing the sp^2 carbons and the atoms or groups attached to them.

Since the two electrons of the π bond are not present axially between the carbon atoms, they are not 'on average' as close to the nuclei of the atoms as the electron pair in the bond. Therefore, they are not

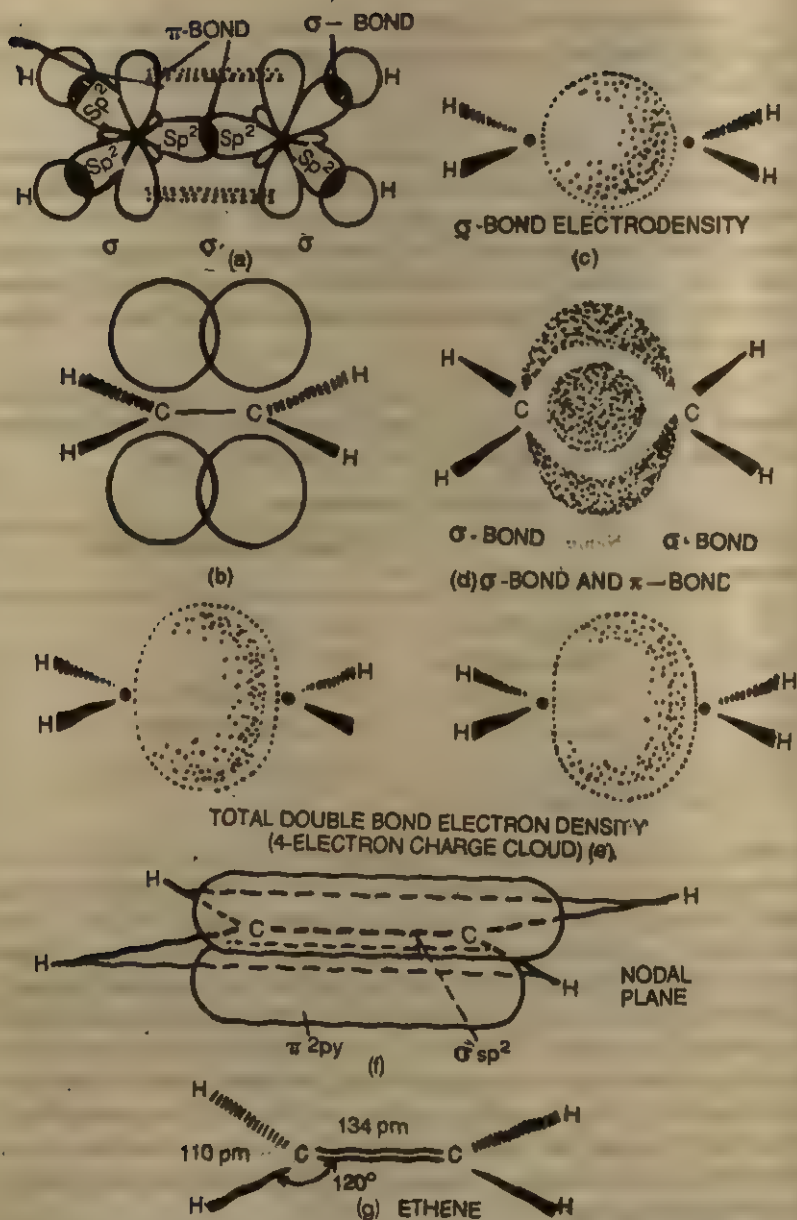


Fig. 16.19. (a), (b), (c), (d), (e) (f) and (g) Sigma (σ) and pi (π) bonds formation through overlap of orbitals in ethene molecule.

attracted by the nuclei very strongly, so the π bond is not as strong as the σ bond. Nevertheless, the σ and π bonds together are stronger than the single σ bond that combines the carbon atoms in ethane. As a

result the $C = C$ bond in ethene is stronger and shorter than the $C - C$ bond in ethane. The bond energies of a $C - C$ single bond (σ bond) and $C = C$ double bond (σ bond plus a π bond) are 347 and 588 kJ mol^{-1} respectively. This is also reflected in the reduced distance between the two carbons. Now the question arises as to why are alkenes more reactive than alkanes if double bonds are stronger than single bonds. When bromine adds across the double bond, the π bond is broken which requires energy. The amount of energy used in breaking the π bond, however, is more than the energy released during the formation of two new bonds to bromine atoms. Hence, alkenes are energetically unstable with respect to their products in an addition reaction. Further, they are kinetically unstable, because the high electron density between the carbon atoms tends to attract electron deficient groups (called electrophiles), thus initiating addition reactions.

The overlap of p-orbitals on adjacent carbon atoms restricts the rotation about the σ bond between these two carbon atoms. If rotation is to take place, sufficient energy ($\sim 280 \text{ kJ mol}^{-1}$) must be made available to dissociate the π bond (Fig. 16.20a). This restricted rotation imposed by the π bond prevents attached groups from changing position relative to one another and results in geometrical isomers. (Fig. 16.20 b).

The inability of rotation about a carbon-carbon double bond is further justification for the orbital overlap model of covalent bonding, for if overlapping of orbitals leads to stability, reduction of overlapping, required in rotation, should require considerable energy.

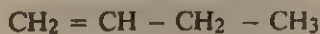


16.6.1 Isomerism in Alkenes

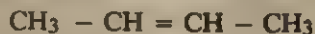
If the π bond can assume more than one position in the molecule, isomers are possible and the position of π bond is indicated by a number the name of alkene. Ethene and propene do not possess structural isomers, as the ways of representing propene are identical.



However, the double bond may be positioned differently in C_4H_8 .



1 - Butene



2 - Butene

The relative rigidity about the $C = C$ double bond leads to geometrical isomerism. For example, we may show the two structures for 2-butene as given in Fig. 16.20. The two compounds have exactly the same atoms bonded to the same atoms, so they are not structural isomers,

but the arrangements of the atoms in space are different. Because of the difference in their geometry, they are called geometrical isomers.

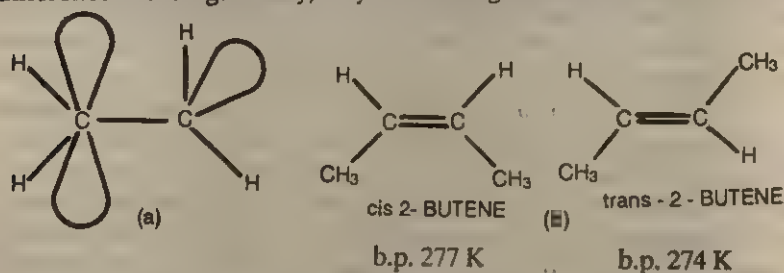
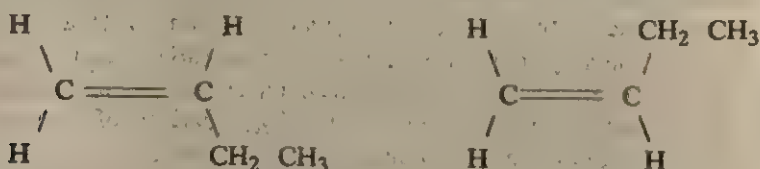


Fig. 16.20 (a) The π bonds of an alkene must dissociate for the rotation to occur about the $C - C \sigma$ bonds.

(b) the restricted rotation imposed by the π bond suggests the possibility of geometrical isomers.

In general, the trans isomer is more stable. If the two substituents on a carbon atom containing the double bonds are the same, then that molecule cannot exist as geometrical isomers, e.g., 1-butene, does not have any geometrical isomer:



Hence, in order to exhibit geometrical isomerism, the two substituents on each carbon atom comprising the $C = C$ double bond of an alkene must be different.

16.7 ALKYNES

Alkynes are hydrocarbons that contain a triple bond between two carbon atoms. The simplest alkyne is ethyne, C_2H_2 , which is commonly called acetylene.

Members of the alkyne family with their condensed structural formulae are listed in Table 16.2. Their general formula is C_nH_{2n-2} . The names of all alkynes end in "____yne".

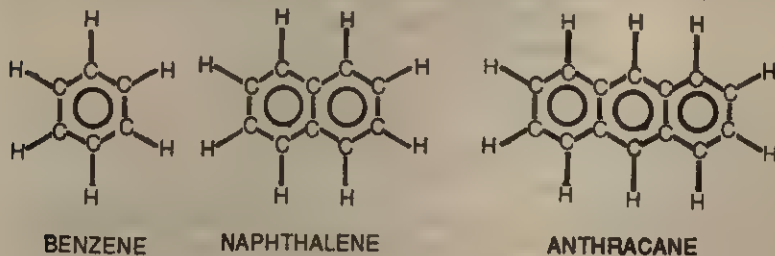
TABLE 16.2 Simple alkynes

Molecular formula	Name	Condensed structural formula
C_2H_2	Ethyne (acetylene)	$HC \equiv CH$
C_3H_4	Propyne (methyl acetylene)	$CH_3 - C \equiv CH$
C_4H_6	2-Butyne (dimethyl acetylene)	$CH_3 - C \equiv C - CH_3$
C_5H_8	2-Pentyne (ethyl methyl acetylene)	$CH_3 - CH_2 - C \equiv C - CH_3$

The triple bond in alkynes can be thought of as consisting of a bond and two π bonds. As in ethene, in ethyne the σ bond frame work of the molecule is formed by the axial overlap of two sp hybrid orbitals; the π bonds are each formed by the overlap of two 2p orbitals (Fig. 16.21). Because the 2p orbitals are at right angles to one another and have two lobes each, the two π bonds have four regions of negative charge around the C - C bond. These regions form a cylindrical sheath of electron density about the C - C σ bond. The triple bonding is reflected in the bond energy (829 kJ) and in the $\text{-C} \equiv \text{C-}$ bond length (120 pm). The structure provides no possibility for isomerism. Since ethyne has no lone pairs, its molecule is linear. The two π bonds of the alkynes behave in the same manner as the π bond of the alkenes. With a high density of electron in the triple bond, ethyne may be expected to attract electrophiles and undergo addition reactions like those of ethene. It is kinetically more stable than ethene.

16.8 ARENES

In the earlier two sections, we considered unsaturated compounds with double and triple bonds. There is another important class of unsaturated compounds called arenes. All arenes are cyclic compounds. The alkanes, alkenes alkynes and their cyclic relatives are known as aliphatic hydrocarbons. This word is derived from the Greek word aliphatos meaning oil or fat. Arenes are also called aromatic hydrocarbons because of the fragrance of several of the members of this class. The term aromatic is now used in the context of their chemical properties, and some aromatic compounds are hardly considered fragrant at all. Benzene is the simplest aromatic hydrocarbon. Monocyclic arenes like benzene (C_6H_6) have the general formula $\text{C}_n\text{H}_{2n-6}$; bicyclic arenes like naphthalene (C_{10}H_8) conform to $\text{C}_n\text{H}_{2n-12}$ and in general, an arene with m rings has the formula $\text{C}_n\text{H}_{2n-6m}$. Despite the fact that arenes are unsaturated, they behave differently from alkenes and alkynes in their chemical reactions. Some simple arenes with their structures are given below:



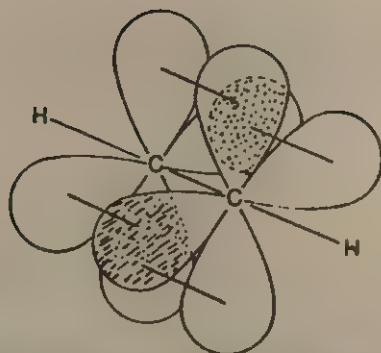
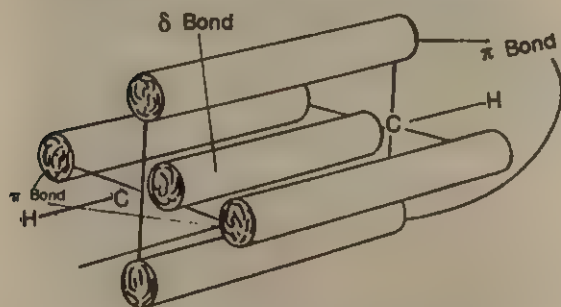
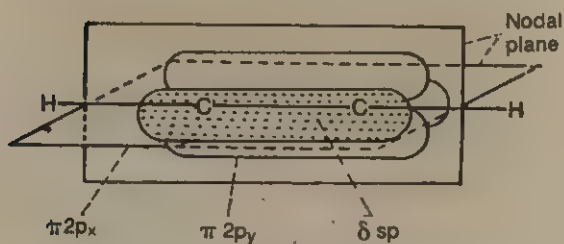


DIAGRAM SHOWING OVERLAP OF PORBITALS OF
ETHYNE



THREE-DIMENSIONAL REPRESENTATION. LIMITED REGIONS
OF BONDING ORBITALS SHOWN.



ACETYLENE, SHOWING sp HYBRID SKELETON
WITH $\pi 2p_x$ and $\pi 2p_y$ ORBITALS OF TRIPLE BOND
LINEAR CONFIGURATION OF ACETYLENE

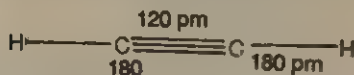


Fig. 16.21. Sigma (σ) and Pi (π) bonds formation through the overlap of orbitals in the ethyne molecule.

16.8.1 The Structure of Benzene

The molecular formula of benzene has been known since 1834 to be C_6H_6 . The exact structural formula, however, posed a problem for many years. Kekule (1865) was the first to propose a ring structure for benzene and in which alternate carbon atoms were joined by double bonds, (Fig. 16.22)

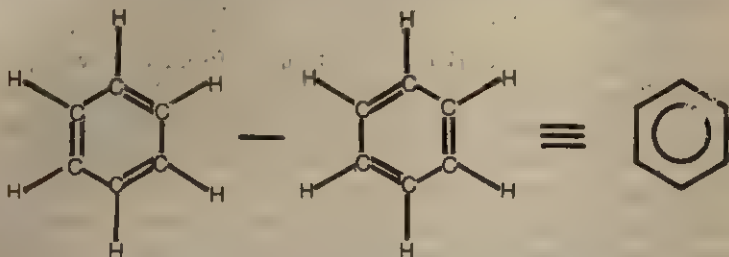


Fig. 16.22. Benzene, the double bonds are not fixed

This structure, called the Kekule or cyclo-hexatriene structure, explains many of the properties of benzene and was accepted for a long time. But even this structure leaves some problems.

(i) Benzene having three double bonds should behave like a highly unsaturated compound, but actually it is found to behave like a saturated hydrocarbon, forming substitution compounds readily.

(ii) Kekule formula contains two kinds of bonds, single and double bonds between carbon atoms. Therefore, it is expected to have different bond lengths between its carbon atoms, i.e., $C-C$, 154 pm and $C=C$, 134 pm. In fact, from X-ray studies it has been found that all the bonds of benzene are of equal lengths (139 pm) and the bond angle $C-C-C$ is 120° .

(iii) Kekule formula admits the formation of two disubstituted products for similar substituents e.g., the two o-dichlorobenzenes possible would be :



However, only one o-dichlorobenzene is known.

To overcome these objections, Kekule suggested that the double bonds in benzene ring oscillate between two possible structures. The true representation of benzene is a resonance hybrid of the two forms shown in Fig. 16.22

The observed $C - \hat{C} - C$ bond angles, 120° can be explained in terms of sp^2 hybridization of carbon atoms leaving one pure $2p$ orbital on each carbon atom.

C (normal) : $1s^2, 2s^2, 2p_x^1, 2p_y^1$

C (excited) : $1s^2, 2s^1, 2p_y^1, 2p_x^1, 2p_z^1$

The carbon framework of the molecule is formed by overlap of sp^2 hybrid orbitals. The three sp^2 hybrid orbitals on each carbon atom are used to form two sigma bonds with the adjacent carbon atoms and one with an hydrogen atom (Fig. 16.23). The six unhybridized (or pure) $2p$ orbitals, each having one electron, are perpendicular to the plane of the molecule and they are close enough to permit a lateral overlap of their electron clouds, yielding six extended π bonds (Fig. 16.24). It should be emphasized here that the extended π bonds are delocalized on all the carbon atoms.

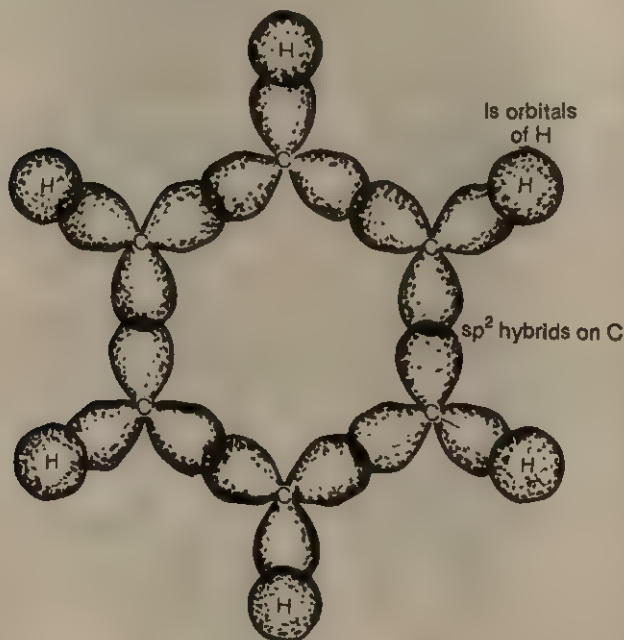


Fig. 16.23. The formation of carbon skeleton of benzene.

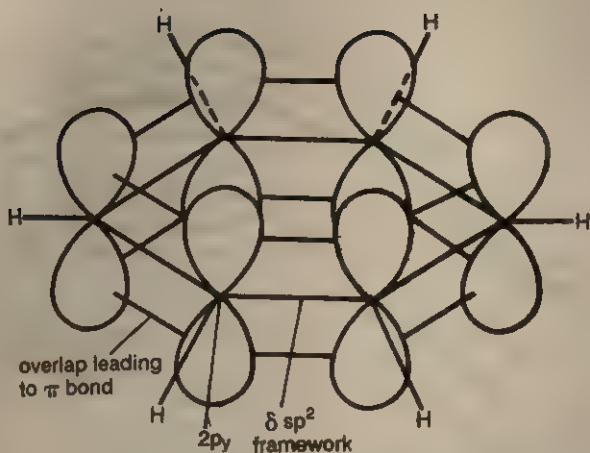


Fig. 16.24. Overlap of $2p_y$ orbitals leading to formation of extended π -orbital systems in benzene.

This is illustrated in Fig. 16.26, where we see the σ bonds as the solid lines between the carbons and the π bonds as a donut-shaped cloud with electron density above and below the carbon ring.

The two resonance structures of benzene would be formed by the overlap of pairs of adjacent p orbitals, as shown in Fig. 16.25.

The electrons in these π orbitals form a symmetrical cloud of electron density above and below the plane of the carbon atoms. Such a

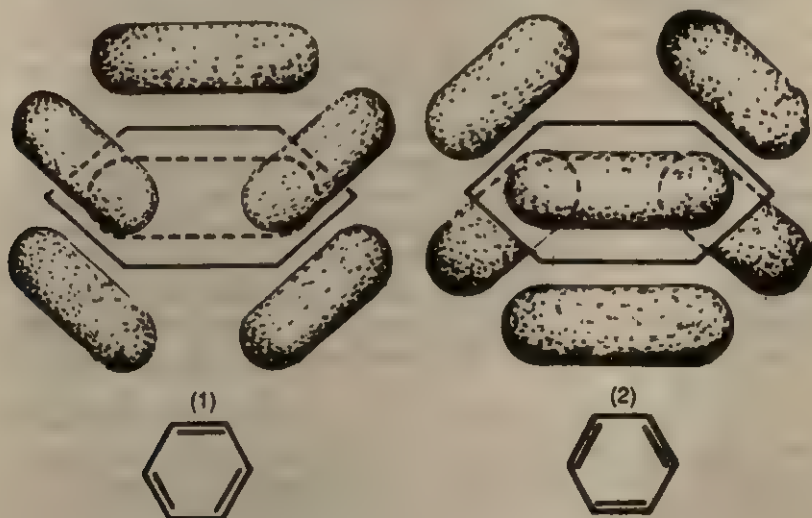


Fig. 16.25. Valence bond resonance structures of benzene

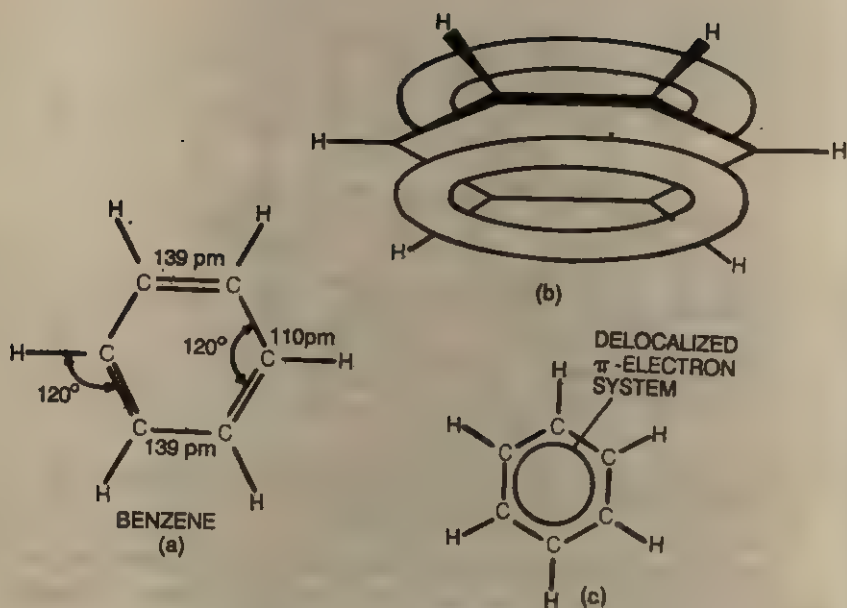


Fig. 16.26. Benzene molecule (a) carbon skeleton with bonds. (b) π electron cloud distribution in benzene (c) delocalized π electron system.

system of delocalized π bond is represented by a circle within the hexagon of six carbon atoms (Fig. 16.27).

The delocalization of the π electron cloud in benzene leads to a very stable ring structure. In fact, thermochemical calculations show that benzene is more stable than the hypothetical 1,3,5-cyclohexatriene by approximately 150kJmol^{-1} . Any system in which electron delocalization can occur is stabilized. This is because of the fact that electrons tend to repel one another, so a system in which they are as far apart from one another as possible they will enjoy minimum repulsion and will, therefore, be stabilized. The behaviour of π electrons in benzene and other aromatic compounds is significantly different from that of π electrons in alkenes and alkynes. The rigid stability also explains its resistance to undergo chemical reactions. It is also responsible for substitution reactions because addition reactions would disturb the π electron cloud of benzene molecule.

The structure described above means that the benzene molecule is planar, symmetrical and non-polar. The absence of polarity explains its liquid nature at room temperature and immiscibility with water. Its boiling point is 353K and its melting point is 279K. Its high boiling point is because of the fact that highly symmetrical benzene ring can pack into crystal lattice.

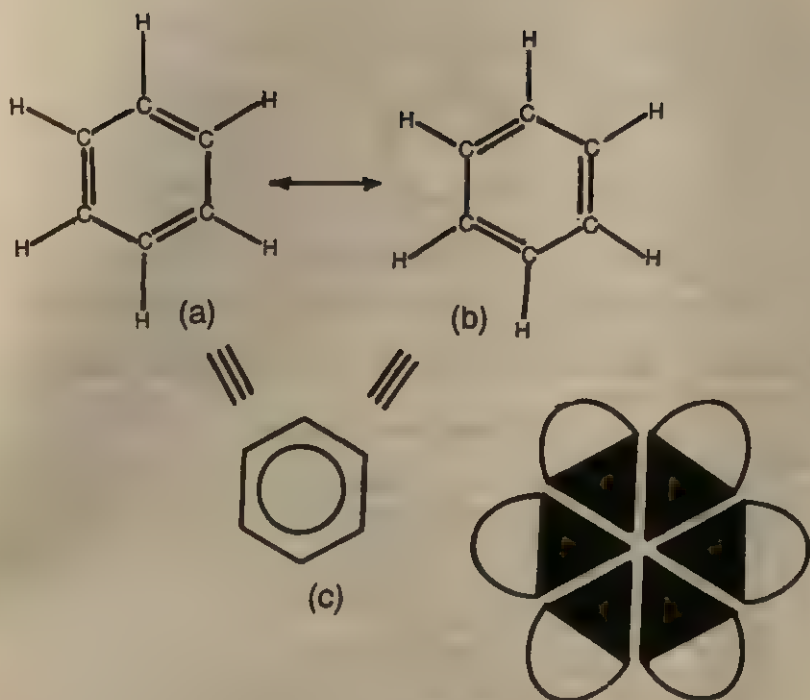


Fig. 16.27 Structure of benzene

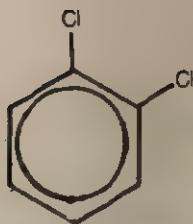
Scale Model

16.8.2 Resonance

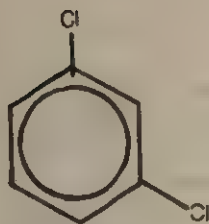
In terms of the Kekule structures, benzene may be described as a resonance hybrid of the two structures, (a) and (b) as shown in Fig.16.27. A double headed arrow is the symbol used to indicate resonance between the two structures. Resonance between equivalent structures (e.g. the Kekule structures) leads to considerable stabilization (i.e. lowering of energy). Benzene is thus a molecule stabilized by resonance energy which is estimated to be about 150 kJ mol^{-1} . In recent years, benzene is more frequently represented by the graphic formula (c) in which the hexagon shows the carbon skeleton and the circle represents the delocalized π electrons.

16.8.3 Isomerism in Arenes

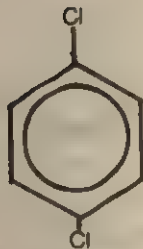
In benzene, which is a symmetrical molecule, all hydrogens are equivalent. It, therefore, forms only a single monosubstitution product. However, it forms three disubstitution products, e.g., the three dichlorobenzenes:



1,2 - Dichlorobenzene
or
(ortho - dichlorobenzene)



1,3 - Dichlorobenzene
or
(m - dichlorobenzene)



1,4 - Dichlorobenzene
or
(p - dichlorobenzene)

when three or more positions in benzene are substituted, the number of isomers would be more.

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

16.1. Put tick (✓) mark against the correct answer.

- (i) An organic compound will show optical isomerism if,
 - (a) all groups attached to C - atom are same.
 - (b) two groups attached to C - atom are different
 - (c) three groups attached to C - atom are different
 - (d) four groups attached to C - atom are different.
- (ii) Isomers of a substance must have the same
 - (a) structural formula
 - (b) physical properties
 - (c) chemical properties
 - (d) molecular formula.
- (iii) Tetrahedral nature of bonding in carbon atom was first shown by
 - (a) Kekule
 - (b) Van't Hoff and Le Bel
 - (c) Lewis
 - (d) Wohler.
- (iv) Which of the followings is closer to bond angle in ethylene molecule ?
 - (a) 90°
 - (b) $109^\circ 5'$
 - (c) 180°
 - (d) 120°
- (v) In the series, ethane, ethylene and acetylene the C-H bond energy is:
 - (a) greatest in ethane
 - (b) nearly the same in all the three compounds
 - (c) greatest in ethylene
 - (d) greatest in acetylene.
- (vi) Geometrical isomerism is possible in case of
 - (a) pentane
 - (b) propene
 - (c) 2-butene
 - (d) ethane
- (vii) Resonance is due to
 - (a) delocalization of sigma electrons
 - (b) delocalization of pi electrons
 - (c) migration of H atoms
 - (d) migration of protons.
- (viii) When the solution of a substance rotates, the plane of plane polarized light to the left side, it is
 - (a) dextro rotatory
 - (b) laevorotatory
 - (c) racemic mixture
 - (d) optically inactive.
- (ix) Which of the following statements is wrong ?
 - (a) a pi bond is weaker than a sigma bond.
 - (b) a sigma bond is weaker than a pi bond
 - (c) a double bond is stronger than a single bond.
 - (d) a covalent bond is stronger than a H-bond.
- (x) Benzene is essentially a resonance hybrid of the two Kekule structures, Hence,
 - (a) half of the molecules correspond to one structure, and the other half to the second structure.
 - (b) an individual benzene molecule changes back and forth between two structures.
 - (c) at low temperatures, benzene can be separated into the two Kekule's structures.
 - (d) the two structures make equal contribution to the resonance hybrid.

16.2 Fill in the blanks

- (i) Organic compounds in which the carbon atoms are linked in open chains are called compounds, whereas those in which they are linked together in a special unsaturated ring arrangement are called compounds.
- (ii) are compounds that have the same molecular formula but different structural formulae.
- (iii) The common C — C bond in which there is end-to-end overlap of the orbitals is called a bond, whereas additional C — C bonds obtained from lateral (sidewise) overlap of orbitals are called
- (iv) Compounds with carbon atom exist in two forms whose molecules are mirror images or enantiomers.
- (v) Enantiomers rotate polarized light in opposite directions and are called

16.3 Indicate by writing true (T) / false (F) against each sentence.

- (i) Pi electron cloud of benzene provides stability to the benzene ring.
- (ii) Electron in π orbitals are not accessible to electron seeking reagents (electrophiles).
- (iii) Benzene is a planar, symmetrical molecule, with each carbon atom lying at the corner of a regular hexagon.
- (iv) Superimposable mirror images are termed enantiomers.
- (v) The alkenes are generally chemically more reactive than the alkanes.
- (vi) The chair form of cyclohexane is less stable than its boat form.
- (vii) Achiral objects are those which are superimposable on their mirror images.
- (viii) In the eclipsed conformation of ethane all the C — H bonds of one methyl group are aligned with those of the second.

SHORT ANSWER QUESTIONS

- 16.4 (i) What is meant by electron delocalization in benzene ?
- (ii) What is a racemic mixture ? How does it differ from meso forms of the molecule ?
- (iii) What are the types of bonds present in alkenes and alkynes ?
- (iv) What are conformers ?
- (v) What is a chiral molecule ?

TERMINAL QUESTIONS

- 16.1 What is meant by isomerism ? Describe the various types of isomerism.
- 16.2 Give the structural formulae and names of the isomers with the molecular formula (a) C_5H_{10} and (ii) C_5H_8 .
- 16.3 Give the structural formulae of the following cycloalkanes: (i) cyclopropane, (ii) cyclobutane, (iii) cyclopentane, and (iv) cyclohexane.
- 16.4 Write a detailed note on the strain theory applied to cycloalkanes.
- 16.5 Discuss the structure of benzene
- 16.6 (a) Cis-trans isomerism is encountered in olefins and cycloalkanes. Explain.
- (b) How many structural isomers are possible for C_4H_8 ? Which will show geometrical isomerism ?
- 16.7 Which of the followings will show geometrical isomerism ?
- (i) 2-pentene, (ii) 1-chloropropene, (iii) 1-chloro-2-methyl-2-butene, (iv) 1-pentene.
- 16.8 (a) Is it proper to say that absolutely free rotation exists in carbon-carbon single bond ? Why ?
- (b) Alkenes and cycloalkanes have the same general formula. In what important ways they differ in their structure ?
- 16.9 (a) Is it correct to say that benzene is saturated ?
- (b) Explain why was it difficult to assign a structure of benzene in agreement with its properties ?
- 16.10 Draw the chair and boat conformation of cyclohexane.
- 16.11 Pick up the primary, secondary and tertiary carbons in the followings
- 2-Methyl-3-ethylhexane; 3,3-Trimethylheptane; 3-Isopropylhexane.
- 16.12 Account for the following observations:

- (i) Carbon-carbon bond length in ethane is 154 pm.
- (ii) Carbon-carbon bond length in ethylene is 134 pm.
- (iii) Carbon-carbon bond length in benzene is 139 pm.

ANSWERS TO SELF ASSESSMENT QUESTIONS

- 16.1 (i) d, (ii) d, (iii) b, (iv) d (v) b (vi) c (vii) b (viii) b (ix) b (x) d
- 16.2 (i) aliphatic; aromatic (ii) isomers, (iii) sigma; pi (iv) asymmetric (v) optical isomers
- 16.3 (i) T (ii) F (iii) T (iv) F (v) T (vi) F (vii) T (viii) T
- 16.4 (i) In benzene, the π orbitals are able to overlap all round the ring. The electrons in the p orbitals cannot be regarded as located between any two carbon atoms; they are free to move between all the carbon atoms in the ring. They are described as delocalized and are represented as an annular cloud of electron density above and below the plane of the molecule.
- (ii) A mixture of equal quantities of the (+) and (-) forms is optically inactive and is called a racemic mixture and is designated by the (\pm) sign. They can be separated. The process of separation is called resolution. Certain molecules with chiral centres show a non-chiral configuration. They have a plane of symmetry. These stereoisomers are called the meso forms. They cannot be resolved into optically active enantiomers.
- (iii) Alkenes contain a double bond which includes one σ and one π bond. Alkynes contain a triple bond which includes one σ bond and two π bonds.
- (iv) In a ethane molecule, each methyl group can be rotated with respect to the other without affecting the σ bond. The different structures which are obtained by this rotation are called conformers.
- (v) A compound with an asymmetric carbon atom is said to possess chiral centre, and hence, a chiral molecule.

Preparation and Properties of Hydrocarbons

Most of the substances belonging to our globe are constantly undergoing alterations in sensible qualities, and one variety of matter becomes as it were transmuted into another....

Such changes, whether natural or artificial, whether slowly or rapidly performed, are called chemical; thus the gradual and almost imperceptible decay of the leaves and branches of a fallen tree exposed to the atmosphere, and the rapid combustion of wood in our fires, are both chemical operations....

The object of Chemical Philosophy is to ascertain the causes of all phenomena of this kind, and to discover the laws by which they are governed.

SIR HUMPHRY DAVY (1812)

UNIT PREVIEW

- 17.1 Introduction
- 17.2 Sources of hydrocarbons : origin of coal and petroleum, hydrocarbons from coal and petroleum, cracking and reforming, octane number.
- 17.3 Laboratory preparation of alkanes
- 17.4 Laboratory preparation of alkenes
- 17.5 Laboratory preparation of alkynes
- 17.6 Physical properties of alkanes
- 17.7 General nature of organic reactions
- 17.8 Chemical reactions of alkanes
- 17.9 Properties and reactions of alkenes
- 17.10 Properties and reactions of alkynes
- 17.11 Reactions of arenes : (aromatic hydrocarbons)
- 17.12 Orientation in electrophilic substitution

LEARNING OBJECTIVES

At the completion of this unit, you should be able to:

- 1. Describe the sources of hydrocarbons
- 2. Define hydrocarbon, alkane, alkene, alkyne and arene.
- 3. Differentiate between aliphatic and aromatic hydrocarbons.
- 4. Give the principles and processes of isolation of hydrocarbons from coal and petroleum.
- 5. Describe the industrial processes of preparing hydrocarbons.
- 6. Describe the laboratory methods used for preparation of aliphatic hydrocarbons.
- 7. Correlate the general trends in physical properties of hydrocarbons with their structures.
- 8. Describe a few important chemical reactions of hydrocarbons such as substitution, addition and oxidation.
- 9. Explain the acidic character of acetylene.

17.1 INTRODUCTION

The large family of organic compounds containing only the elements carbon and hydrogen is appropriately named the hydrocarbons. Hydrocarbons are of importance because they may be considered as the basis of all the organic compounds. Replacement of hydrogen atom in a hydrocarbon by an -OH group gives an alcohol; a -COOH group gives a

carboxylic acid. It is the presence of groups such as these in the molecules that produces the dominant chemical characteristics of substances. A substance is what it is - that is, it behaves as it does chemically - because of the presence of one or more functional groups. Thus, all organic compounds can be looked on as being derived from the hydrocarbons. There are two types of hydrocarbons aliphatic and aromatic.

17.2 SOURCES OF HYDROCARBONS

Plants and animals continued to be the rich source of organic compounds until the beginning of 19th century. In recent years, petroleum, natural gas and coal have become the important sources of organic compounds, particularly, hydrocarbons.

17.2.1 Origin of Coal and Petroleum

Coal is a black mineral of vegetable origin (fossil material). As the plants died, they were buried under ground (swampy and marshy in nature). The cycles of decay, new growth and decay created vast deposits of plant material. In time, carbonization (a process which takes place in the absence of air) of vegetable matter took place and coal formed. During the course of carbonization, several varieties of coal are formed.

Petroleum is a mixture of different hydrocarbons (solid, liquid as well as gaseous). It has no uses in its raw form. It derives its name from the latin words 'Petra' (meaning rock) and 'oleum' (meaning oil).

Petroleum (or crude oil) is black viscous liquid with a characteristic smell. It occurs under the earth's crust entrapped in impervious rocks (Fig. 17.1). It was formed from the decomposition of the remains of marine animals and plants that were buried in the beds of Fig. 17.1 Oil

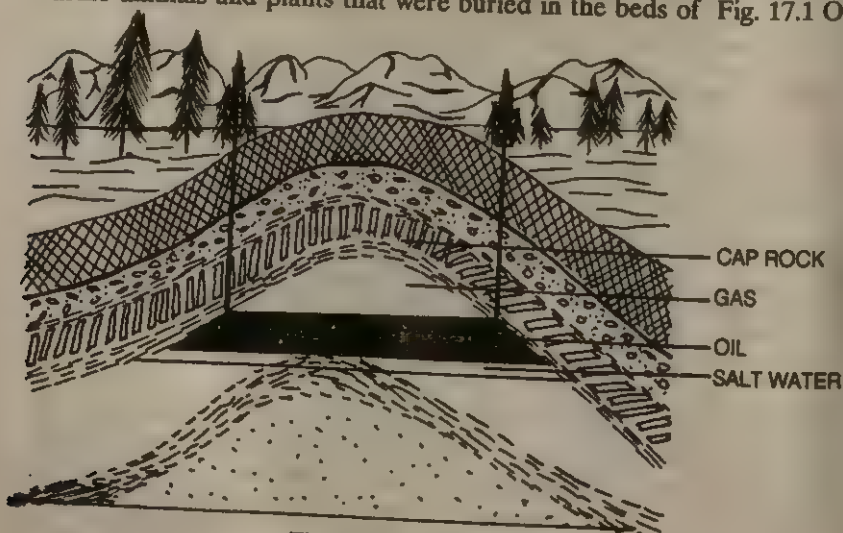
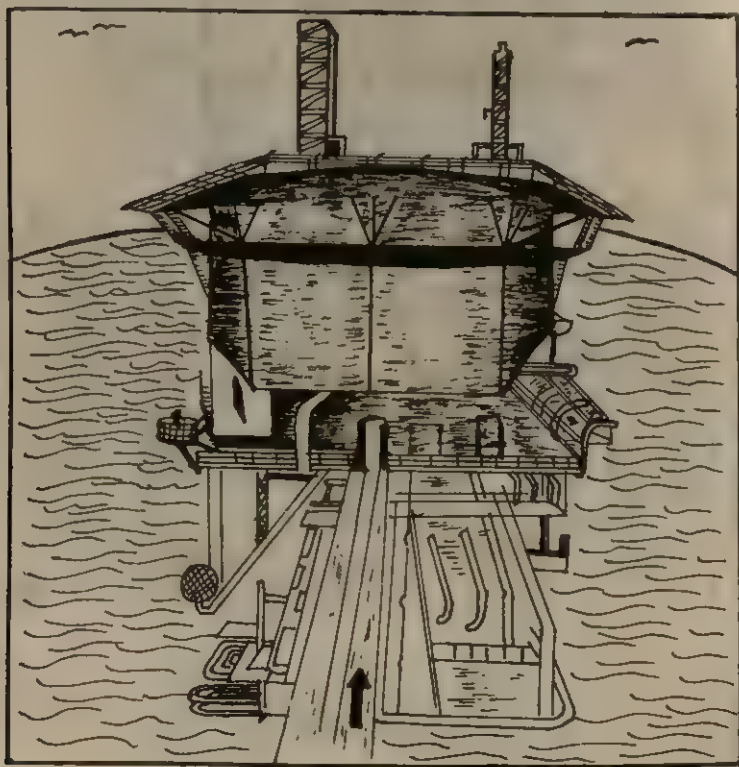
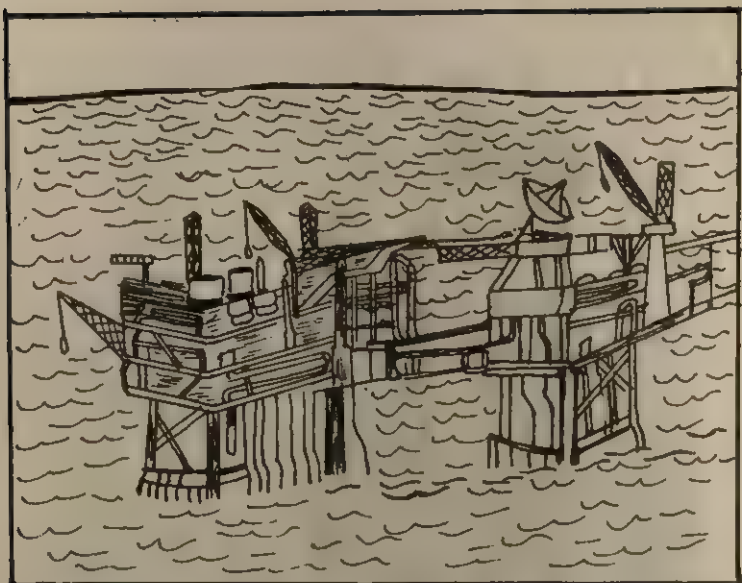


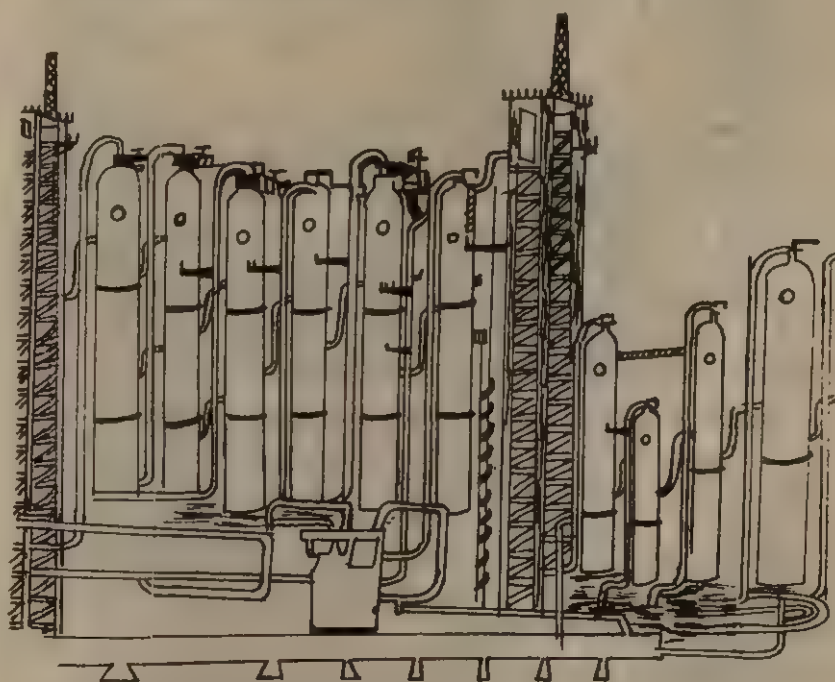
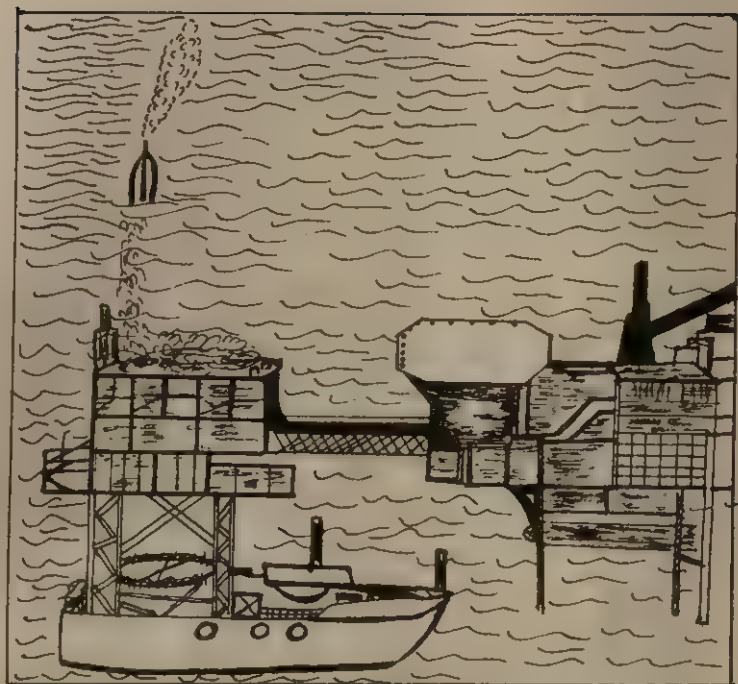
Fig. 17.1 Oil bearing rocks



17.1 (b) A view of an oil refinery



17.1 (c) Offshore activities of the Bombay High



17.1 (d) Towers and access elevators in the Process Unit

bearing rocks the seas millions of years ago. These animals and plants had, by the process of photosynthesis, made sugars and other organic compounds that they required to sustain life. During the course of time, high pressures and temperatures and bacterial action converted these compounds into oil. Similar conditions led to the formation of the natural gas that is often found associated with crude oil as well as in deposits of its own.

Over the years coal has proved to be the richest source of energy. It affects the economy of a country to a large extent. Coal is found in abundance in our country under the earth at the depth of ~ 300 m. The big coal mines in our country are in the eastern states of the country, i.e., Bihar (Jharia and Bokaro) and West Bengal (Raniganj). Coal mining began in India at Raniganj in West Bengal in 1774. After independence in 1947, the coal mining industry was stepped up. The chief coal producing countries (other than India) of the world are China, USA, USSR, UK, Germany, Poland and Australia.

The United States of America is the biggest oil producer in the world followed by Russia, Venezuela, Mexico, Rumania, Iraq and some other middle east countries. India is a poor producer of petroleum. Although the oil production in India has been increased considerably during the last few years but the demand for petroleum and its products is also increasing with the increase in the number of automobiles, aeroplanes, diesel engines, tanks, tractors, etc.

Oil and Natural Gas Commission (ONGC) is the main government agency set up in 1956 for exploration and production of oil both from on-shore and off-shore areas in the country. Its significantly recent achievement is the production of crude oil from 'BOMBAY HIGH' in Maharashtra. Another new organisation called, Oil India Limited (OIL) was established by the government in 1981. Initially, this organisation started its activities in the eastern region of our country but recently extended to Mahanadi basin and parts of Rajasthan.

The chief oil producing centres in India are : Rudrasagar and Lakwa in Assam; Ankleshwar and Kalol in Gujarat and Bombay High (off - shore area). Petroleum is obtained by drilling holes into the earth's crust where the presence of oil is anticipated. The depth of petroleum deposits vary from place to place. The oil well has to be drilled until the oil-bearing region is reached. The crude oil, thus, obtained is transported to refineries where it is processed.

17.2.2 Composition of Coal and Oil

Coal is mainly composed of carbon. During the course of carbonization several varieties of coal, such as, peat, lignite, bituminous

and anthracite are formed. These varieties of coal differ in free carbon content. Anthracite (hard coal) may contain as much as 95% of free carbon. Bituminous (soft coal) contains about 65% carbon. The various compounds present in coal are given in Fig. 7.2 (Unit 7). Crude oil mainly consists of aliphatic hydrocarbons with much lesser amounts of aromatic compounds and organic compounds of sulphur and nitrogen.

17.2.3 Aromatic Hydrocarbons From Coal

Coal is a commercial source of arenes. When coal is destructively distilled (*i.e.*, strong heating in the absence of air) four main products are obtained: coal gas, ammoniacal liquor, coal tar and coke. The other materials obtained from these sources are shown in Fig. 7.2. (Unit 7). The residual mass is called coke.

The volatile ammonia is absorbed in acid which, in turn, is used for manufacturing ammonium salts and fertilizers. Fractional distillation of coal tar gives various aromatic hydrocarbons (Table 17.1). Coke is used as a source of carbon for reduction of metal oxides in metallurgy (*e.g.*, in the iron and steel industry). It can be converted to graphite. It is a valuable fuel.

Coal gas is an important fuel. It contains lower hydrocarbons—alkanes and alkenes.

TABLE 17.1 Fractions of Coal Tar

Fraction	Temperature range(K)	Composition
Crude oil(light oil)	upto 443	Benzene, toluene, xylene
Middle oil (carbolic oil)	443-503	Phenol, Cresol naphthalene
Heavy oil or (cresote oil)	503-543	Methyl and higher alkyl benzene, cresols
Green oil or (anthracene oil)	543-633	Naphthalene, anthracene, etc.
Pitch		Used for surface roads and in the manufacture of asphalt roofing.

Hydrocarbons From Petroleum (Oil Refining)

Crude oil or petroleum obtained from the oil well is a complex mixture of hydrocarbons. It has no use in the raw form. It is processed in refineries. In India, oil refineries are located at Koyali, Bombay, Cochin, Vishakhapatnam, Haldia, Barauni, Guwahati, Digboi and Mathura.

Refining of Petroleum

Refining of Petroleum is the process by which various useful products are separated from water, earth particles present in crude oil. To start with, crude oil is washed both with acidic and basic solutions. Refining is done by a process known as fractional distillation (Unit 18). It is an efficient method of separating petroleum into fractions based on the difference in the boiling points of the fractions.

In fractional distillation, the vapours of the crude oil are made to rise through a packed fractionating tower. The vapours of higher boiling

point (i.e., less volatile) liquids condense in the lower part while the lower boiling liquids (more volatile) condense in the upper parts. Trays are fitted at different heights to collect various fractions (Fig. 17.2). The fractions obtained can further be fractionally distilled. The list of the fractions is given in Table 7.14 (Unit 7).

17.2.5 Cracking and Reforming

The petroleum fractions with 1 to 12 carbon atoms in the molecules are in great demand in large quantities than the fractions with bigger molecules. Keeping in view the increasing demand, techniques have been developed to increase the availability of these fractions.

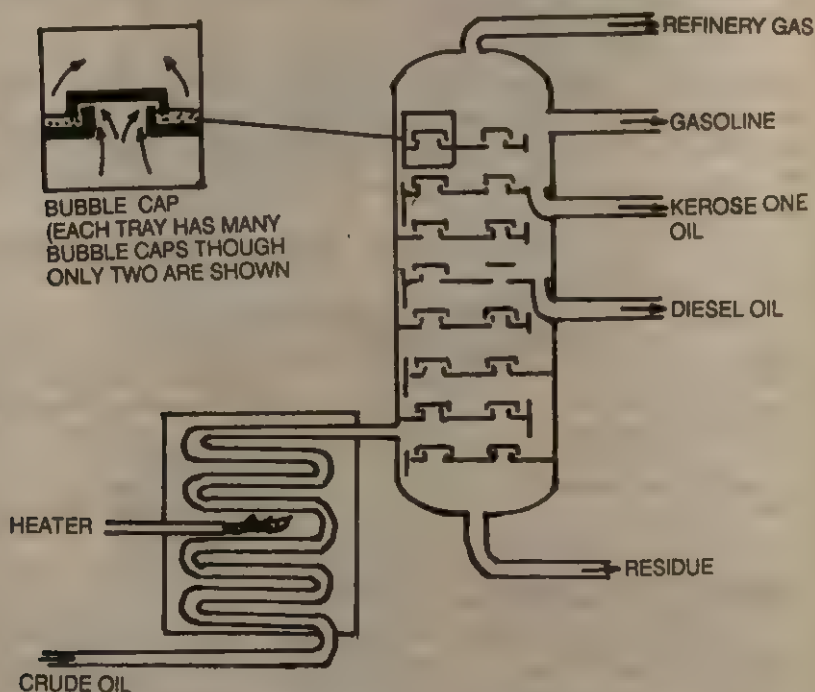
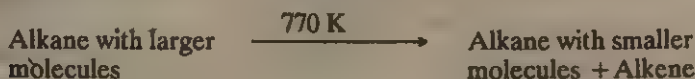


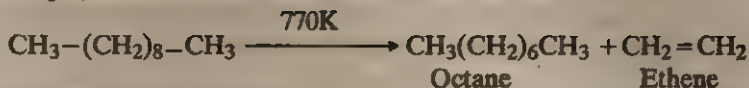
Fig. 17.2 Fractional distillation of petroleum (crude oil)

Cracking

The petroleum industry uses pyrolysis (splitting by heat) of high molar mass alkanes to give hydrocarbons with smaller molecules. On heating, the molecules of alkanes vibrate strongly and finally their C - C bonds break to give smaller molecules, one of which is alkene. For example,



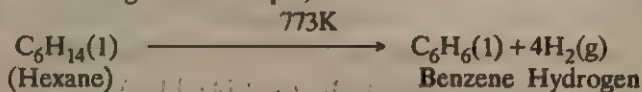
For example,



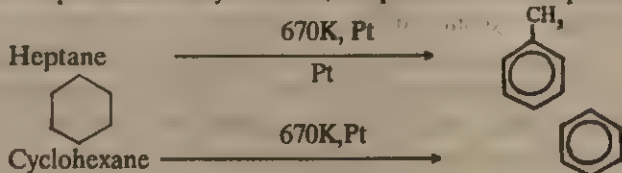
Such reactions are known as cracking. Thermal cracking is difficult to control and give rise to complex product mixtures. By using a catalyst, $\text{Al}_2\text{O}_3/\text{SiO}_2$, cracking can be made to occur at fairly low temperatures (600-650K). This is known as catalytic cracking. This process is very important in petroleum industry. It is used to produce extra gasoline from kerosene fraction. Further, cracking tends to produce branched chain rather than straight chain alkanes, and therefore, gasoline of high octane rating. It is also a source of industrially important alkenes such as ethene, propene and butene.

Reforming

It is a process in which straight chain and cyclic alkanes are effectively broken up and then reassembled as branched chain molecules and aromatic rings. For example,



Some other catalysts like palladium, platinum or nickel are also used. If a platinum catalyst is used, the process is called platforming.



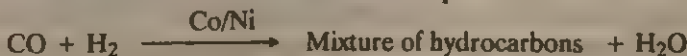
The process helps in converting low grade gasoline to high grade fuel.

17.2.6 Aliphatic Hydrocarbons from Coal

Coke, one of the pyrolysis products of coal, on reacting with steam gives water gas.

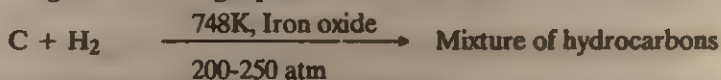


When water gas, mixed with more of hydrogen, is passed over heated cobalt or nickel (as catalyst), a mixture of hydrocarbons is produced. This reaction is called Fischer-Tropsch reaction.



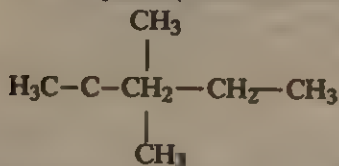
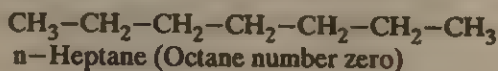
The mixture of hydrocarbons is separated by the usual methods of separation.

According to another process called Bergius process, powdered coal is hydrogenated at 748K at 200-250 atm in the presence of iron oxide, when a high octane rating liquid fuel is obtained.



17.2.7 Quality of Gasoline-Octane Number

Gasoline or petrol is the most important of all the fractions because of its increasing demand for propelling automobiles and aeroplanes. Its vapours mixed with air are ignited by an electric spark in the cylinder of a motor car engine. As a result, an explosive reaction takes place producing energy. This energy provides the power for propelling the vehicle. The rate at which this reaction occurs and the ease with which it is initiated are very important for the efficiency of the engine. If the explosion occurs too fast, energy will be dissipated instead of being converted to useful kinetic energy. If the explosion starts too early, the piston experiences 'knocking'. Fuel containing straight chain alkanes such as heptane ignite very readily and explode very rapidly, causing 'knocking' and inefficient combustion. Fuel containing branched chain alkanes such as 2,2,4-trimethylpentane (iso-octane) is more efficient and like to cause less knocking. The octane rating of 2,2,4-trimethylpentane is set at 100 and that of heptane (burns explosively with knocking) at zero. A mixture of these two standards has been found to produce the same knocking as the gasoline under test, the percentage of iso-octane in this mixture is the octane number of the gasoline. Thus, the gasoline mixtures rich in branched chain alkanes burn smoothly and efficiently in high performance engines and have high octane numbers.



2,2,4-Trimethylpentane (Octane number 100)

A mixture of tetraethyl lead (TEL) and ethylene dibromide is also used for the purpose. When burned TEL produces small particles of lead oxide which tend to combine with free radicals produced in the chain reaction of combustion, thus, slowing it down and making it smoother. Ethylene dibromide prevents the accumulation of lead in the engine by forming lead bromide, which is volatile and is swept away in the car exhaust.

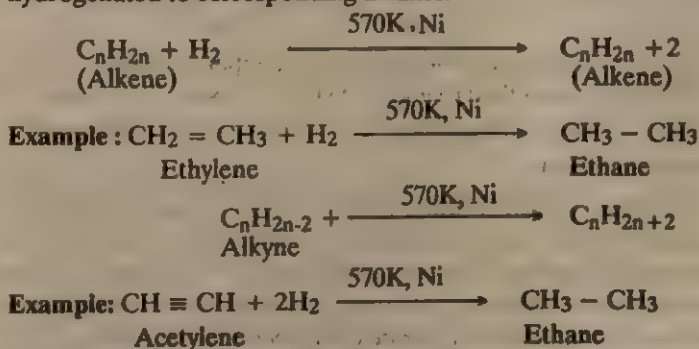
Alongwith lead, gasoline engines discharge other pollutants into the atmosphere – carbon dioxide, carbon monoxide, nitrogen oxides, sulphur dioxide and unburnt hydrocarbons. Carbon monoxide is very toxic as it forms a stable compound with haemoglobin in the blood; making the haemoglobin unable to transport oxygen. Accumulation of lead in the blood may cause brain damage. Oxides of nitrogen and unburnt hydrocarbons take part in the complex sequence of chemical reactions that leads to the occurrence of photochemical smog (Unit 12). Efforts are on to phase out the use of lead gasoline. Methods to oxidize the unburnt hydrocarbons and carbon monoxide to carbon dioxide are being tried.

17.3 LABORATORY PREPARATION OF ALKANES

Petroleum is the richest source of hydrocarbons including alkanes. Some of the lower alkanes are manufactured by cracking of hydrocarbons with high molar mass. Some laboratory methods normally used for the preparation of alkanes are given in this section.

17.3.1 From Unsaturated Hydrocarbons by Catalytic Hydrogenation

When alkenes or alkynes mixed with hydrogen are passed over finely divided nickel (or palladium or platinum) at about 570K, they are hydrogenated to corresponding alkanes.



Hydrogenation reactions are used in the manufacture of vanaspati ghee and edible vegetable oils.

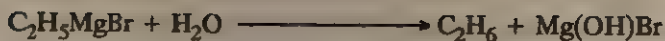
17.3.2 From Alkyl Halides

The hydrogen in alkyl halides, RX can be replaced by hydrogen using a number of methods:

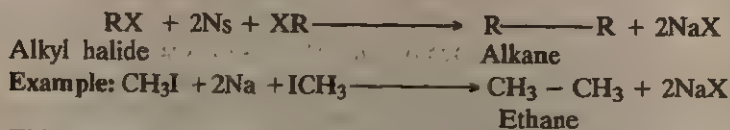
(i) Using Grignard Reagent: Alkyl halides react with magnesium metal present in diethyl ether forming alkyl magnesium halides (Grignard reagents).



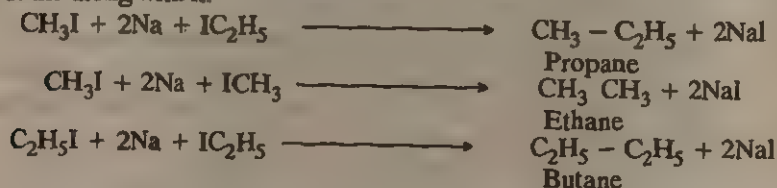
This compound readily reacts with compounds such as water and acids can easily donate protons. An alkane is produced.



(ii) **Wurtz Reaction:** The alkyl halides (preferably bromides and iodides) react with metallic sodium in presence of dry ether to produce alkanes.

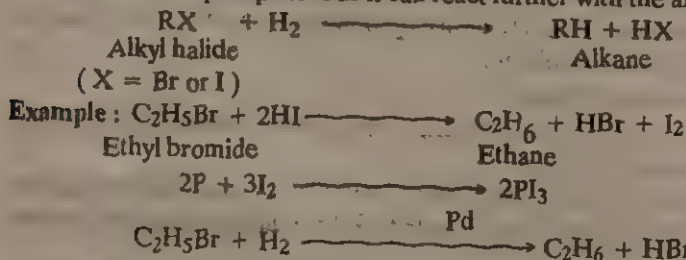


This method is suitable for the preparation of symmetrical alkanes. A mixture of products is obtained when two different alkyl halides are taken. Thus, if one wants to prepare propane, a mixture of methyl iodide and ethyl iodide in equimolecular proportions are reacted with sodium. This will not only product propane but will also produce ethane and butane along with it.



Now to get pure propane, mixture is to be separated. Hence, this method is of limited use in the laboratory. The reaction is more useful to prepare alkanes with odd numbers of carbons as a mixture of hydrocarbons is obtained.

(ii) **Reduction of Alkyl Halides :** Various reducing agents are used for the purpose. All give the same products. Alkyl halides are reduced with either red phosphorus and hydriodic acid or hydrogen in the presence of a catalyst. Iodine produced in the reaction is removed by reaction with red phosphorus as it can react further with the alkane.

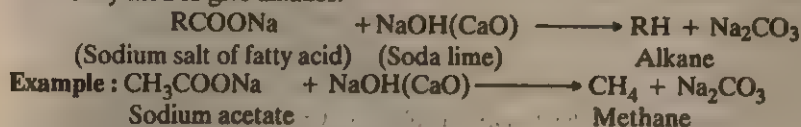


The reaction may also be performed by using zinc and hydrochloric acid or by reducing with lithium aluminium hydride, LiAlH_4 . The reaction of ethyl alcohol on Zn-Cu couple supplies nascent hydrogen which can also work as a reducing agent.

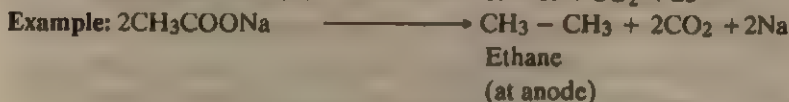
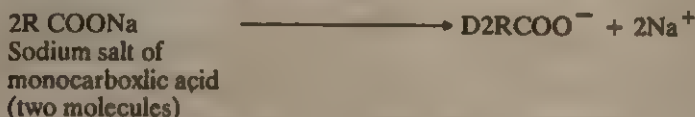
17.3.3 From Carboxylic Acids

Two methods are usually used for the preparation of alkanes from carboxylic acids.

(i) **By Decarboxylation** : The removal of COO^- is termed decarboxylation. The sodium salts of alkyl carboxylic acid (where R = alkyl group) on heating with soda lime ($\text{NaOH} + \text{CaO}$) are decarboxylated to give alkanes.

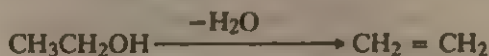


(ii) **By Kolbe's Electrolytic Method** : When an aqueous solution of sodium or potassium salt of monocarboxylic acid is electrolyzed, a higher alkane is obtained at the anode.



17.4 LABORATORY PREPARATION OF ALKENES

Natural petroleum and gas, together with coal, provide much of the world's requirement of organic chemicals in general and hydrocarbons in particular. Alkenes are the important compounds. They are used in manufacturing a large number of organic compounds. They are generally synthesized by elimination reactions. In the course of such reactions the elements of a smaller molecule are eliminated from a single larger molecule. For example,



Here, elimination of water from alcohol results in the formation of ethylene. This reaction is catalyzed by strong acids.

17.4.1 From Alcohols

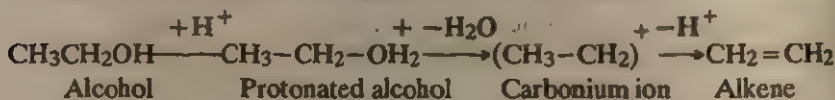
In the laboratory, alkenes are formed by heating ethanol with conc. H_2SO_4 at 443K. It is also named as **dehydration of alcohols**. The dehydration of alcohols is an important general method for the laboratory preparation of alkenes.

The dehydration may be carried out by either (a) heating with conc. sulphuric acid at 443K or (b) passing the alcohol vapours over alumina, Al_2O_3 at 623–673K. In place of sulphuric acid, H_3PO_4 can also be used.

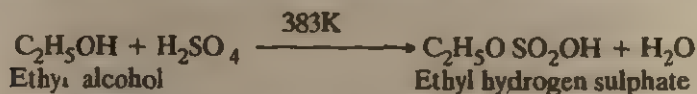
The ease of dehydration of the alcohols is in the order :

Tertiary > Secondary > Primary

The reaction is believed to proceed by initial formation of a protonated alcohol, which dissociates into water and a carbonium ion, the carbonium ion, in turn, loses a proton to yield an alkene.



In the course of dehydration, different products may be obtained depending on the reaction conditions. For example, when dehydration is effected at 383K



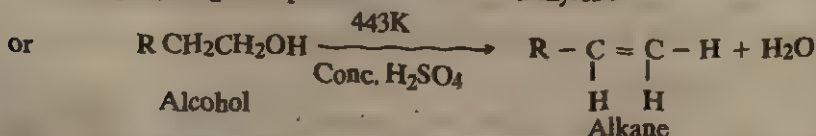
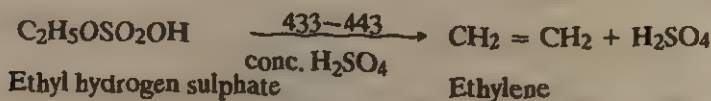
Ethyl hydrogen sulphate can be distilled under reduced pressure to obtain diethyl sulphate.



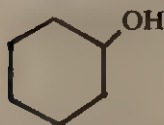
In the course of dehydration, if the temperature used is below 413K and the amount of alcohol used is more than one equivalent of H_2SO_4 , then one molecule of water may be eliminated per two molecules of alcohol, to yield ether.



When heated to 433–443K in the presence of more of H_2SO_4 , it is changed to ethylene.



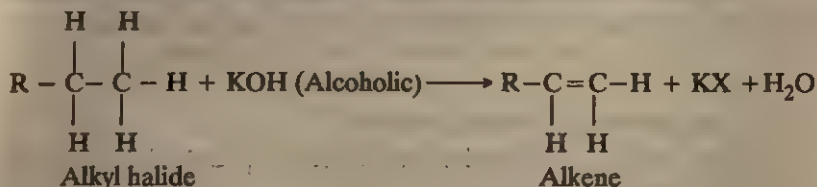
Catalytic dehydration is carried out by passing vapours of alcohol on heated alumina or kaolin at 623 K.



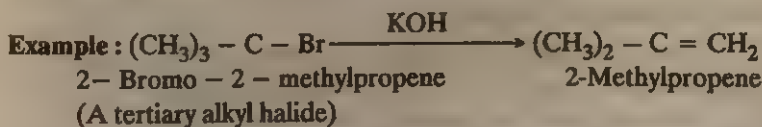
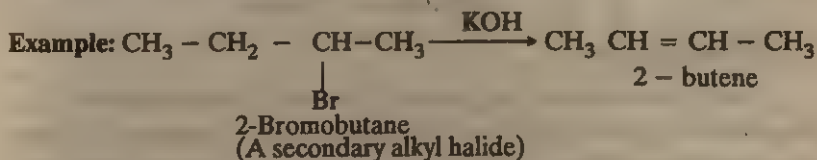
Al₂O₃, 623K

 $+ \text{H}_2\text{O}$

When heated with alcoholic solution of potassium hydroxide, hydrogen halide is removed from alkyl halide giving alkene.

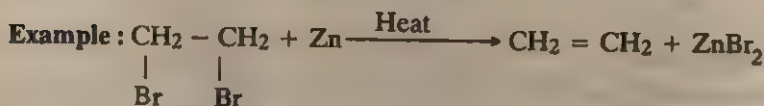


The structure of alkyl halide is also an important factor. Compounds with primary alkyl groups usually give very little alkenes, whereas secondary and tertiary halides, which give highly branched alkenes, give good yields.



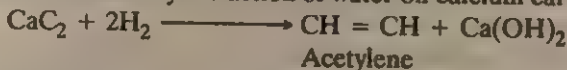
17.4.3 Dehalogenation of Vicinal Dihalides

VA vicinal dihalide is a compound which contains two halogen atoms present on two adjacent carbon atoms. Such compounds on heating with zinc dust gives alkenes.



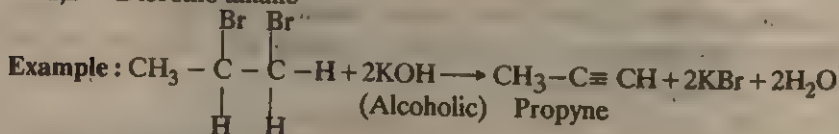
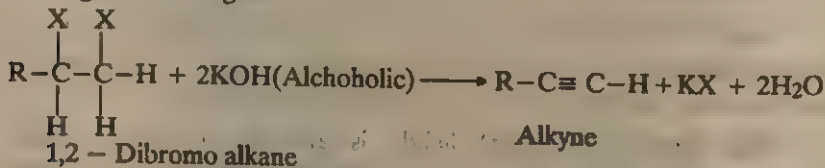
17.5 LABORATORY PREPARATION OF ALKYNES

Acetylene is the most important member in the series. In the laboratory it is obtained by the action of water on calcium carbide.



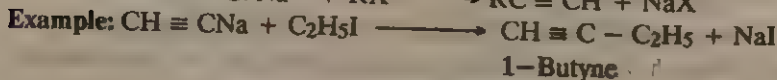
17.5.1 Dehalogenation of Vicinal Dihalides

Vicinal dihalides on boiling with alcoholic potash give acetylene and higher homologues.



17.5.2 From Acetylene

Higher homologues are generally prepared from acetylene. For this acetylene is first treated with sodium metal in presence of liquid ammonia when sodium acetylide is produced, which on treatment with alkyl halide yields higher alkynes.



17.6 PHYSICAL PROPERTIES OF ALKANES

The alkanes form a homologous series and the members show a gradual change in physical properties as the number of carbon atoms in their molecules increases. This has already been seen in the distillation of crude oil which is chiefly composed of alkanes. Some properties of individual straight chain alkanes are given in Table 17.2.

TABLE 17.2 Physical properties of straight chain alkanes

Molecular formula	IUPAC name	State at 398K	Boiling point, K	Melting point, K	Density g/cm ³
CH ₄	Methane	gas	112	90	0.424
C ₂ H ₆	Ethane	gas	184	101	0.546
C ₃ H ₈	Propane	gas	213	85	0.501
C ₄ H ₁₀	Butane	gas	273	138	0.579
C ₅ H ₁₂	Pentane	liquid	309	143	0.626
C ₆ H ₁₄	Hexane	liquid	342	178	0.657
C ₇ H ₁₆	Heptane	liquid	371	182	0.684
C ₈ H ₁₈	Octane	liquid	399	216	0.703
C ₉ H ₂₀	Nonane	liquid	424	219	0.718
C ₁₀ H ₂₂	Decane	liquid	447	243	0.730
C ₂₀ H ₄₂	Eicosane	solid	617	310	0.785

Alkanes are non-polar in nature. They are entirely covalent in nature. Lower members are volatile. The molecular mass determines the volatility of hydrocarbons with the lower members being gases at room temperature and the higher members becoming liquids and solids. Their boiling and melting points rise with increasing molecular mass.

Boiling Point : Table 17.2 shows that for the lower members, a difference of CH₂ corresponds to an increase of about 20 to 30 K in their boiling points.

We know that alkanes are non-polar compounds having weak van der Waals forces of attraction between their molecules. These forces act along the surface of molecule and their magnitude increases with increase in surface area. As the molecular size of alkane increases its surface area increases, thereby an increase in the degree of van der Waals forces is expected. All these factors together explain the increasing trend of boiling point for the homologous series. It is seen that isomeric forms of alkanes show small differences in their boiling points. Generally, branched chain isomers have lesser boiling points than the corresponding normal isomers. For instance, the boiling points of normal pentane and isopentane, are 309 and 301K respectively. This is because of the fact that the branched isomers are comparatively more spherical in shape than unbranched chain hydrocarbons and thus, the attractive forces being more restricted between molecules. The boiling points of a unbranched chain alkanes are plotted against the number of carbon atoms in Fig. 17.3.

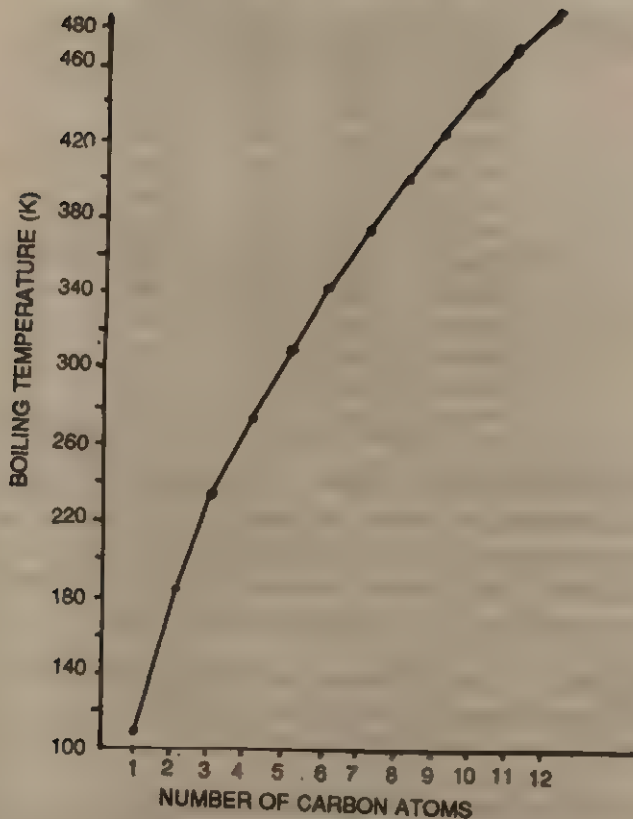
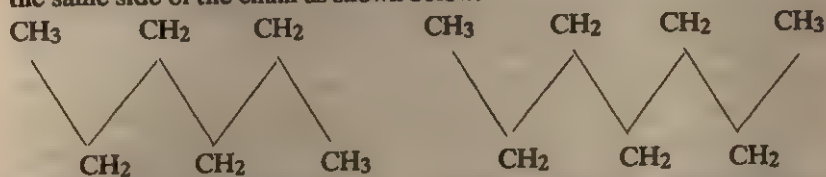


Fig 17.3 Variation of boiling points of hydrocarbons

Alkenes, alkynes, cycloalkanes and arenes also exhibit similar trends in their boiling points. However, unsaturated hydrocarbons possess somewhat higher boiling points than the corresponding saturated hydrocarbons due to greater polarisability of their molecules.

Melting Point: In general, the melting point increases with an increase in the chain length of the carbon atoms in alkanes. However, an alkane with an odd number of carbon atoms has a lower melting point than an alkane with an even number of carbon atoms. (Fig. 17.4) This is due to the fact that the intermolecular forces in a crystal depend not only on the size of the molecules but also upon their arrangement in the crystal lattice. It may be pointed here that the carbon atoms in alkanes do not form straight chains but form rather zig-zag chains. In normal alkanes with even number of carbon atoms, terminal methyl groups are present on opposite side of the zig-zag chain. On the other hand in normal alkanes

with odd number of carbon atoms terminal methyl group are present on the same side of the chain as shown below.



n-Hexane (even number of carbon atoms) (Terminal methyl groups on opposite side of zig-zag chain)

n-Heptane (odd number of carbon atoms) (Terminal methyl groups on same side of the zig-zag chain)

Probably, alkanes with odd number of carbon atoms do not fit so closely in the crystal lattice as the alkanes having an even number of carbon atoms do. Consequently, lower energy is required to break the crystal structure of such alkanes.

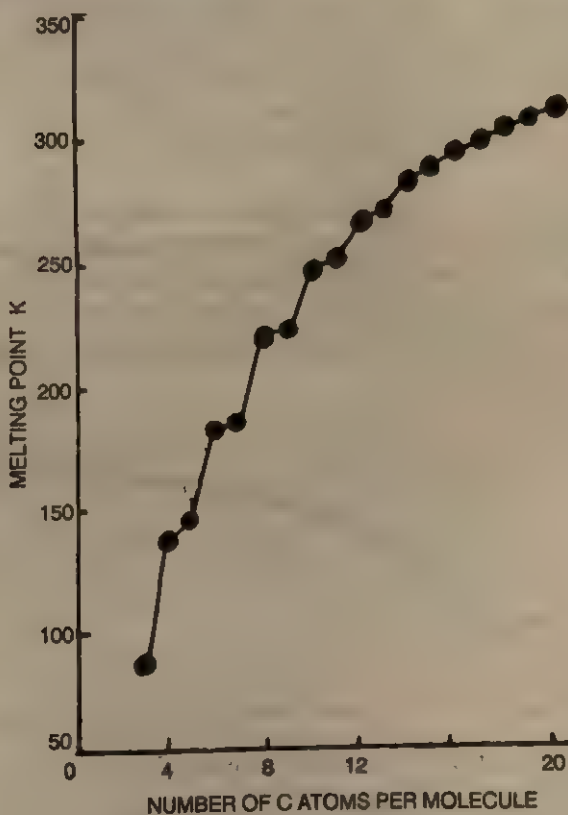


Fig. 17.4 Melting points of alkanes

Alkenes and alkynes also exhibit more or less similar trends in their melting points. However, in case of alkenes, which exhibit geometrical isomerism, the less symmetrical *cis* isomers have lower melting points than the corresponding more symmetrical *trans* forms. For instance, the melting points of *cis* 2-butene and *trans* 2-butene are 134.1K and 167.4K respectively. This is also due to the fact that the more symmetrical *trans* forms adopt compact crystal lattice. Symmetrical arene molecules having higher melting points. For instance, for the three xylenes (O-, m- and p-) the most symmetrical *para* isomer has the highest melting point.

For toluene, the methyl derivative of the highly symmetrical benzene molecule is drastically lower, i.e., m.p. of $C_6H_6 = 278K$; m.p. of $C_6H_5CH_3 = 178K$.

Solubility. Being covalent in character, the hydrocarbons are soluble in non-polar solvents like C_6H_6 , $CHCl_3$, CCl_4 etc. They are insoluble in polar solvents like water. This is in the conformity with the saying "like dissolves like". The liquid hydrocarbons themselves are good solvents for other non-polar substances. They are non-conductors of electricity in solution or molten or vapour state.

Density: The density of alkanes increases with increase in the size of the molecule (Fig. 17.5) but reaches the limiting value of about $800kg\ m^{-3}$ ($0.8g\ cm^{-3}$). They are less dense than water: oil floats on water. The higher members are viscous liquids; the viscosity increases with increasing molecular mass as the attractive forces between molecules increase.

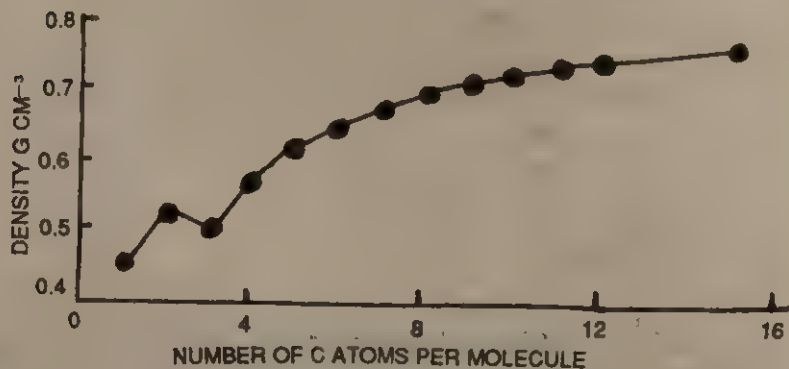


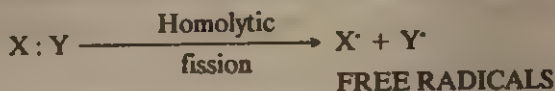
Fig. 17.5 Densities of 'n'-alkanes

17.7 GENERAL NATURE OF ORGANIC REACTIONS

17.7.1 Nature of Bond Fission

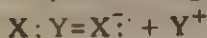
Most of the organic reactions involve the breaking of bond. It depends upon the nature of the covalent bonds. A covalent bond between two atoms, say X and Y of a compound X–Y can be broken in two possible ways.

(i) **Homolytic fission** involves in the breaking of a covalent bond so that each atom retains one of the two electrons of the shared pair.

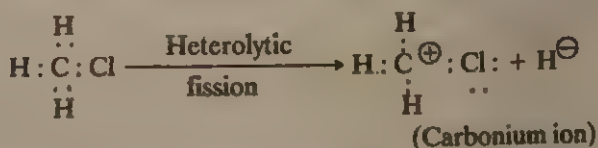


These neutral entities are highly reactive particles and they are known as free radicals. Free radicals are very short-lived. They have a strong tendency to attract an electron from another atom or molecule, reforming an electron pair.

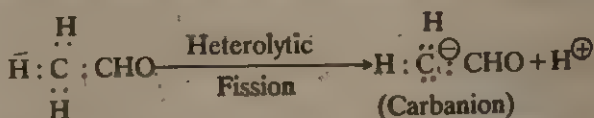
(ii) **Heterolytic fission** involves the breaking of a covalent bond in such way that both the shared electrons are carried away by one of the atoms. This atom will then acquire a net negative charge, while the other atom in the bond will acquire a positive charge.



Carbon atom carrying a positive charge is called carbonium ion and such an ion has only six electrons in the valence shell. For example,



Carbon atom carrying a negative charge is called carbanion ion and such an ion has only six electrons in the valence shell. For example,



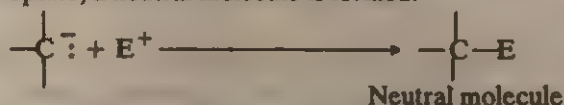
Carbanions constitute important reactions intermediates in organic chemistry.

17.7.2 Nature of Reagents

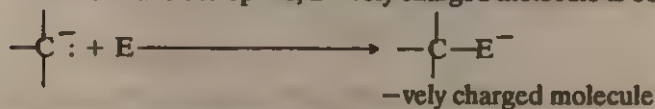
(i) **Electrophilic reagents** : For a large number of reactions it is convenient to call one of the reactants as substrate and the other as attacking reagent. Reagents which are deficient in electrons and take a pair of electrons from the substrate are called electrophilic reagents or

electrophiles (electron- loving). Electrophilic reagents are of two types:

(i) Positive electrophiles, and (ii) neutral electrophiles. The positive electrophiles are those which carry a +ve charge, e.g., H^+ , Cl^+ , NO_2^+ , $\overset{+}{C}$, etc. The neutral electrophiles do not carry positive charge, e.g., BF_3 , $AlCl_3$, SO_3 , etc. When a substrate is attacked by a +ve electrophile, a neutral molecule is formed.

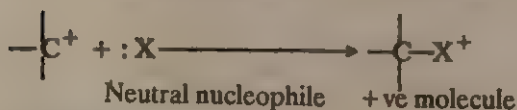
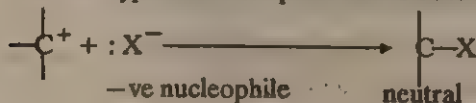


With neutral electrophile, a -vely charged molecule is obtained.



(ii) **Nucleophilic reagents** : Reagents which are rich in electrons and have the tendency to share the pair of electrons with electron deficient substrate are called nucleophilic reagents or nucleophiles. These are of two types: (i) negative nucleophiles, and (ii) neutral nucleophiles. Negative nucleophiles have an electron pair and are negatively charged, e.g., CH_3^- , X^- , CN^- , NH_2^- , etc. Neutral nucleophiles have an electron pair but no -ve charge, e.g., $:NH_3$, H_2O , R_3N , etc.

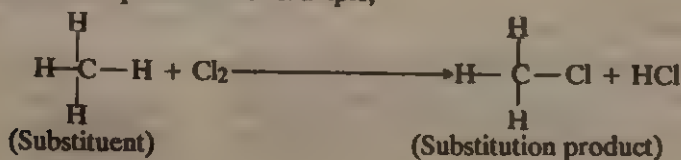
The two types of nucleophiles exhibit the following reactions:



17.7.3 Types of Reactions

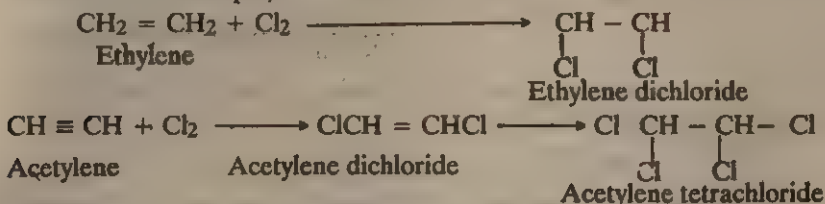
The organic reactions can be conveniently classified into following four categories:

(i) **Substitution reaction** involves the replacement of a hydrogen atom or some other group of a molecule by another atom or group without causing any basic change in the structure of the remaining part of the molecule. The new atom or group which enters the molecule is known as "substituent" and the product so formed is known as "substitution" product. For example,



The substitution reaction may be an electrophilic or nucleophilic type depending upon whether the attacking reagent is electrophilic or nucleophilic in nature. The electrophilic substitution reactions are generally represented as S_E ; while the nucleophilic substitution reactions are represented as S_N .

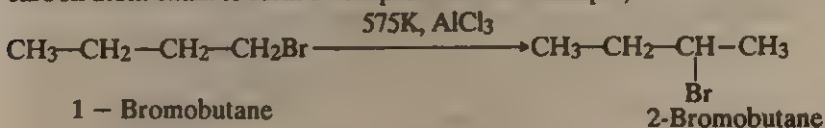
(ii) **Addition reaction** involves the formation of a product by the combination of two or more reacting substances. In addition reactions, one of the reactants always contains a double or triple bond in its molecule. For example,



(iii) **Elimination reaction** involves the removal of atoms or groups of atoms from a molecule yielding compounds containing double or triple bonds. For example,



(iv) **Rearrangement reaction** involves the shifting of a functional group from one atom to another or complete rearrangement of the carbon atom chain to form a new product. For example,



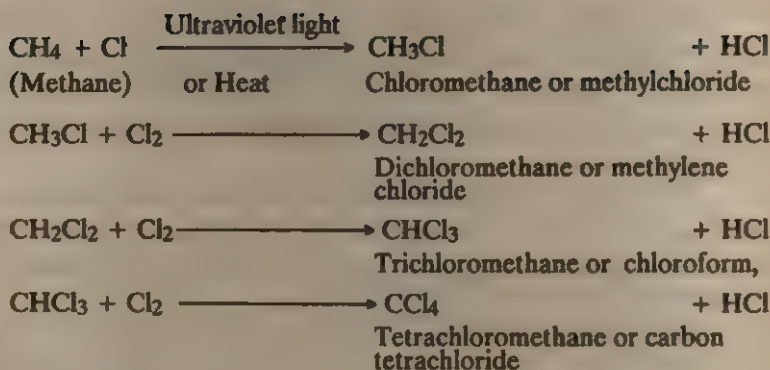
17.8 CHEMICAL PROPERTIES OF ALKANES

Alkanes contain strong sigma single bonds between carbon-carbon and carbon-hydrogen atoms. They are quite inert towards common reagents such as acids, alkalis, oxidizing or reducing agents, *etc.*, under ordinary conditions. Under strong conditions, however, alkanes do undergo a few reactions. Some of such reactions are described below:

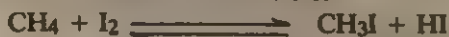
17.8.1 Substitution Reactions

Some of the substitution reactions of alkanes are :

(a) **Halogenation** : When alkanes react with halogens (chlorine or bromine) in the presence of diffuse sunlight (or ultraviolet light) at high temperature (520-670K) or in presence of a halogen carrier (like iron), the H atoms of alkanes are successfully replaced by halogen atoms, *e.g.*,



The reaction of alkanes with flourine is explosive and violent, whereas with iodine it is reversible.



Therefore, direct iodination of alkanes is not possible. However, iodination reaction of alkanes may be brought about in presence of an oxidizing agent such as iodic acid, nitric acid, *etc.*, which oxidize the hydroiodic acid to iodine.



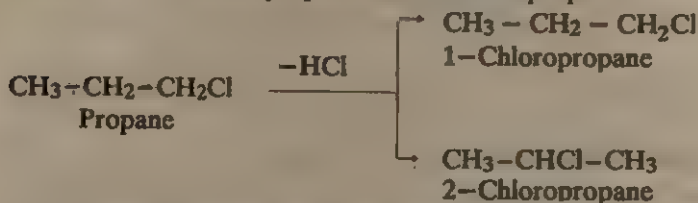
The reactivity of halogens towards alkanes follows the sequence

Flourine >> Chlorine > Bromine >> Iodine

Violent reaction

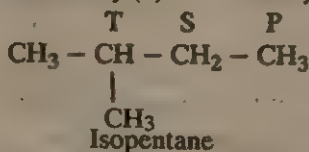
Reversible reaction

Halogenation of higher hydrocarbons yeild a mixture of all possible isomeric halogen derivatives. For example, propane on chlorination gives a mixture of 1-chloropropane and 2-chloropropane.



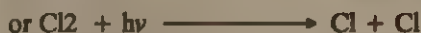
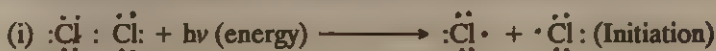
It may be pointed here that different classes of hydrogen atoms, i.e., tertiary, secondary and primary hydrogen atoms are substituted in the following order.

Tertiary (T) > Secondary (S) > Primary (P)



Thus, propane on reacting with Cl_2 gives mainly 2-chloropropane. Mechanism of halogenation involves the following steps:

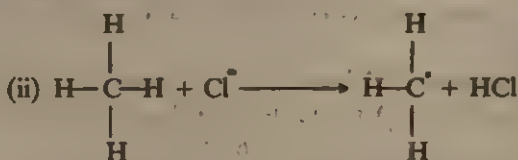
(I) Chain Initiation Step : Since the reaction between methane and chlorine takes place either in the presence of ultraviolet light or organic peroxide (or at 520K), it is believed that halogenation is initiated by the homolytic fission of the chlorine molecules into chlorine atoms. Energy (243kJ) required for this step is supplied by ultraviolet light or by heat.



Chlorine free radicals

Chlorine free radicals bearing high energy are formed by the breaking of covalent bond in the Cl_2 molecule.

(II) Chain Propagation Step : Chlorine free radicals remove a hydrogen atom from methane forming hydrochloric acid molecule and methyl free radical.



Methyl radical

The methyl radicals so produced are also very reactive and react, in turn, with chlorine molecules forming methyl chloride and free chlorine radicals.



Thus, in reactions (ii) and (iii) one free radical is used up and another is formed which can react to generate more free radicals. Such a reaction is called a chain reaction or the propagation step.

As the reaction proceeds the chlorine free radical can also react with methyl chloride molecule to yield hydrogen chloride and substituted methyl radicals.



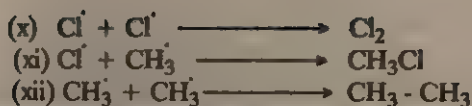
The substituted methyl radical, thus, produced reacts with another molecule of chlorine to form methylene dichloride and chlorine radicals.



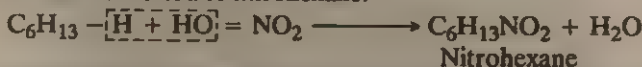
The process may continue until all the hydrogen atoms are substituted leading to the formation of carbon tetrachloride.



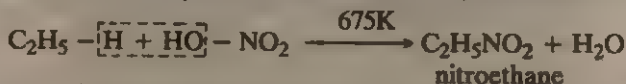
(III) Chain Termination Step : The chain reaction comes to an end when free radicals combine with each other and do not form new free radicals.



(b) **Nitration** : Nitric acid has no action on lower alkanes. When hexane is heated with fuming nitric acid for 48 hours, about 10% of the hydrocarbon is converted to nitrohexane.

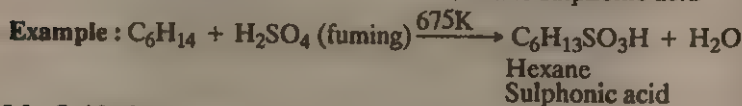
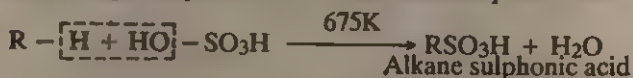


Recently, the "vapour-phase nitration process" has been developed for nitration of alkanes other than methane. For example, when ethane is mixed with nitric acid vapours and heated to 675K, nitroethane is formed.



Some nitromethane (CH_3NO_2) is also produced along with nitromethane.

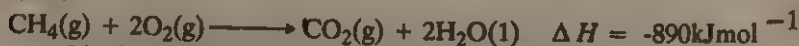
(c) **Sulphonation** : Alkanes, hexane onwards, react with fuming sulphuric acid at high temperatures to form alkane sulphonic acid.



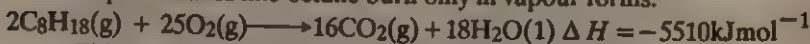
17.8.2 Oxidation

Alkanes are quite unreactive but these, however, can be oxidized. The nature of the products formed depends upon the oxidizing reagent and the conditions of the reaction.

Combustion (burning in excess of oxygen) is the important reaction of the alkanes. They burn with a blue flame forming carbon dioxide and water.

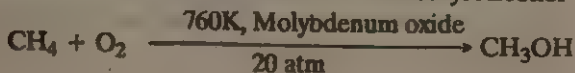
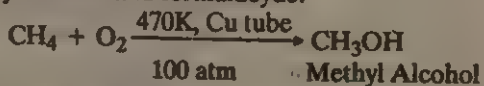


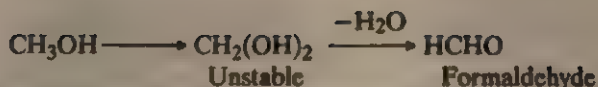
Liquid alkanes like octane burn only in vapour forms.



This reaction takes place in the internal combustion engine.

Normal alkanes may be oxidized under suitable conditions (in presence of a catalyst, high temperature and pressure) to alcohols and aldehydes. For example, catalytic oxidation of methane leads to the formation of methyl alcohol and formaldehyde.

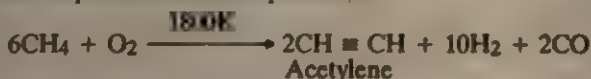




Aldehyde (or ketone) can be further oxidized to an acid and finally to carbon dioxide and water.



They can undergo partial oxidation under appropriate conditions and yield important industrial products.



Elementary carbon in the form of carbon black (used in the type industry, printing ink) is produced in incomplete combustion of natural gas.

17.8.3 Pyrolysis (Cracking)

When the alkanes are heated to 770-875K they decompose. This reaction is called cracking. The nature of product depends on the structure of alkane, presence of a catalyst, pressure and other reaction conditions. For example, propane decomposes at 737K as follows:



The cracking process is believed to proceed by a free radical mechanism as shown below:



Note: Some of the important chemical reactions of alkanes are summarized in Table 17.3. Table also includes a few important methods of preparation.

17.9 PROPERTIES AND REACTIONS OF ALKENES

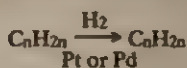
Physical properties of alkenes like melting and boiling points, densities, solubilities, etc., are similar to those of corresponding alkanes. The alkenes with C_2 and C_4 are gases; C_5 - C_{15} liquids; and C_{16} onwards, solids at room temperature.

The carbon-carbon double bond, present in all alkenes, consists of a strong σ bond, and a weak π bond. The electrons of the σ bond are delocalized. This lends the double bond a property of polarizability. Thus, in presence of an attacking agent of alkene molecule undergoes

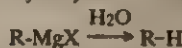
Table 17.3

Preparation of alkanes

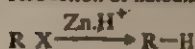
1. Hydrogenation of alkenes



2. Hydrolysis of a Grignard reagent

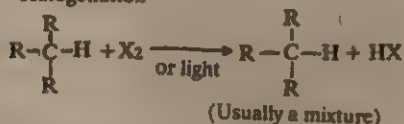


3. Reduction of haloalkane



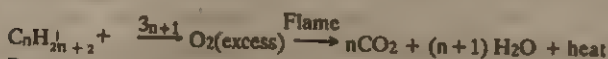
Reactions of alkanes

1. Halogenation

or. Reactivity $X_2 = Cl_2 > Br_2$

$C-H$: tertiary > secondary > primary > CH_3-H

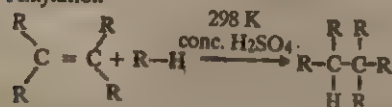
2. Combustion



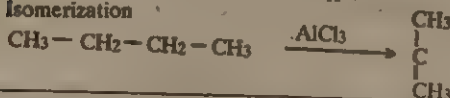
3. Pyrolysis or cracking



4. Alkylation



5. Isomerization



electromeric effect whereby a pair of electrons gets transferred to one of the two carbon atoms and a negative charge is produced on one carbon atom and a positive charge on the other

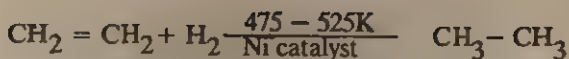


The molecule, thus, develops charged centres by virtue of which it readily attacked by various reagents. In general, alkenes give the reactions of the type given in Section 17.9.1

17.9.1 Electrophilic Additions Reactions

Alkenes readily undergo additions with electrophilic reagents.

(i) Addition of Hydrogen : Hydrogen in the presence of Pt, Ni, Fe, etc., as a catalyst, adds to carbon-carbon double bond.

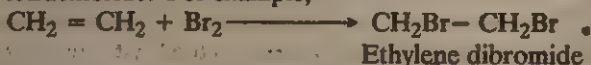


Ethylene

Ethane

Vegetable ghee is manufactured by the hydrogenation of vegetable oil which contains unsaturated hydrocarbons.

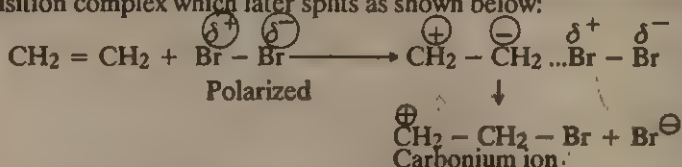
(ii) **Addition of halogens** : Alkenes react with halogens to form dihalides. The order of reactivity is chlorine > bromine > iodine. The reaction is carried out by taking two reactants, usually in an inert solvent like carbon tetrachloride. For example,



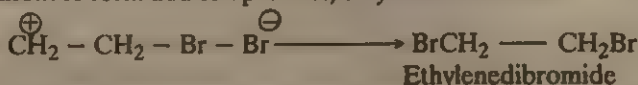
Addition of bromine is extremely useful for the detection of the carbon-carbon double bond. When a 5% solution of bromine in CCl_4 is added to an alkene, it is decolourized.

Mechanism : A halogen molecule is non-polar. However, it becomes polarized on collision with the negatively charged electron cloud of carbon-carbon double bond.

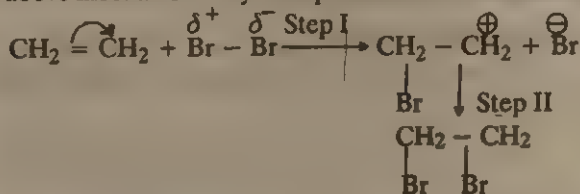
This polarized molecule approaches the ethylene molecule forming a transition complex which later splits as shown below:



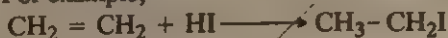
The bromide ion produced then attaches to the positively charged carbon atom to form addition product, ethylene dibromide.



The above mechanism may be represented in brief as follows:

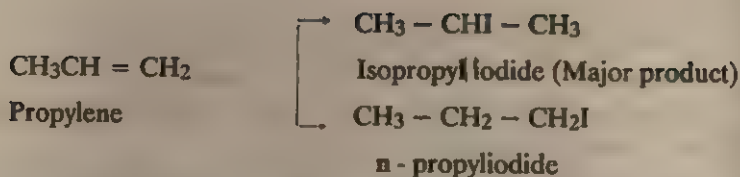


(iii) **Addition of halogen acids** : All halogen acids (HCl , HBr , HI) readily add to alkenes forming alkyl halides. The order of reactivity is $\text{HI} > \text{HBr} > \text{HCl}$. For example,

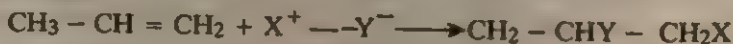


Mechanism : The addition of halogen acids is also a two step ionic process and similar to halogens.

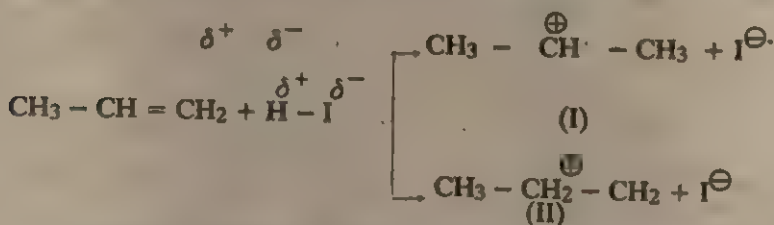
In case of unsymmetrical alkenes the addition of halogen acid (or any other reagent consisting of two different atoms or groups) can result in the formation of two different isomeric products.



Isopropyl iodide has been found to be the main product. Markovnikov (2870) made a careful study on such additions to unsymmetrical alkenes and gave a rule known as "Markovnikov's rule". It states that "the negative part of the molecule adding to the double bond goes to that carbon atom which is linked to the least number of hydrogen atoms". Thus :



Mechanism: The Markovnikov's rule can be understood in terms of ionic mechanism of addition reactions. For example, in the addition of hydrogen iodide to propylene the reaction is initiated by the addition of electrophilic proton to one of the bonded carbon atoms to form either carbonium ion, I or II.

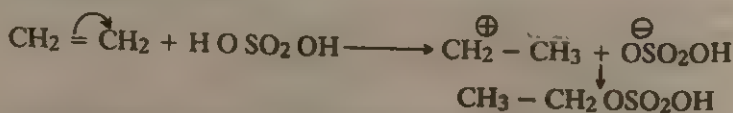


However, the secondary carbonium ion (I) is more stable than the primary carbonium (II). Isopropyl iodide is, therefore, the main product in accordance with Markovnikov's rule.

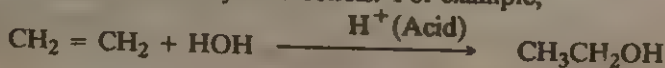
(iv) **Addition of sulphuric acid :** Alkene bubbled through concentrated sulphuric acid is readily absorbed. Alkyl hydrogen sulphate is formed.



The mechanism of this addition reaction is also a two step ionic reaction as illustrated below :



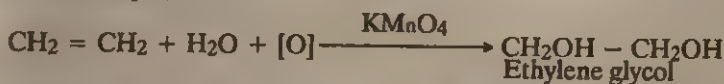
(v) **Addition of water :** Water attacks the double bond in the presence of dilute acids to yield alcohols. For example,



17.9.2 Oxidation of Alkenes

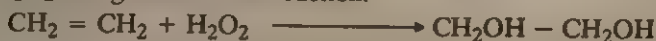
Alkenes are readily oxidized. The nature of products depends upon the type of oxidizing agents.

(i) **With potassium permanganate :** Alkenes on treatment with cold, dilute and slightly alkaline or neutral solution of potassium permanganate are oxidized to dihydroxy compounds called glycols. This reaction is known as "hydroxylation" as it involves the addition of OH-group. For example,

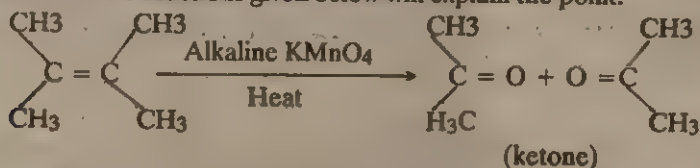


This reaction is used as a test for unsaturation in a compound since potassium permanganate solution gets decolourized (Baeyer's test)

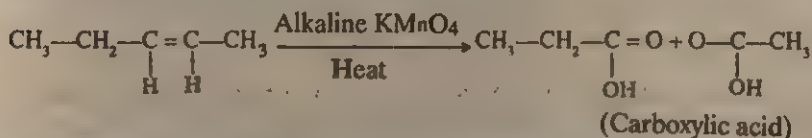
H_2O_2 also gives a similar reaction.



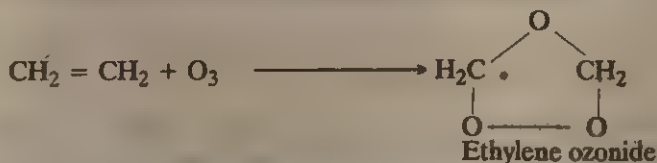
At high temperature, cleavage of the double bond takes place and from the products produced the structure of the unknown alkene can be worked out. Two reactions given below will explain the point.



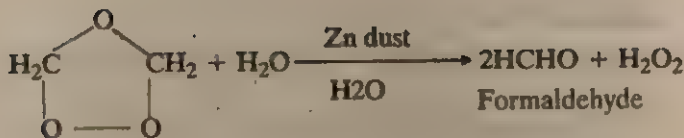
In case a hydrogen atom is attached to the carbon atoms containing a double bond, the hydrogen atom is replaced by a hydroxyl group to form carboxylic acid.



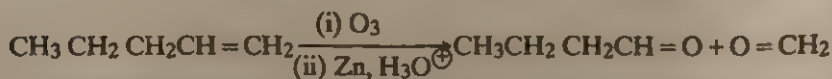
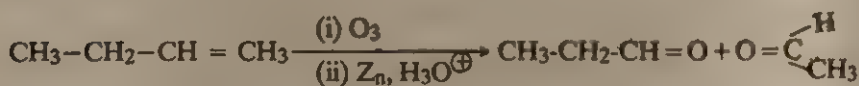
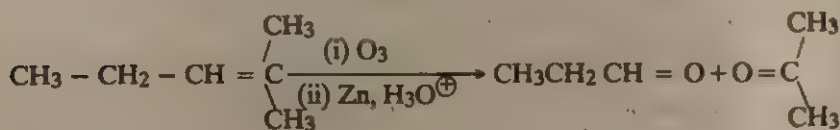
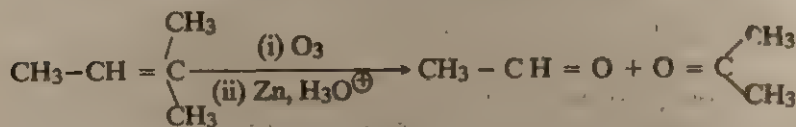
(ii) **With ozone :** When ozone is passed through a solution of alkenes in an inert solvent the latter gets oxidized forming explosive ozonide. This reaction is known as "ozonolysis". For example,



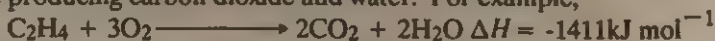
The ozonide, on treatment with water, in presence of zinc dust, undergoes decomposition yielding aldehydes or ketones depending upon the nature of ozonides.



The products, thus, produced can often be used to determine the structure of unknown alkene. The following reactions illustrate the point.

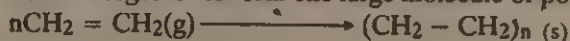


(iii) **Combustion** : Alkenes burn in air or oxygen with a luminous flame producing carbon dioxide and water. For example,



17.9.3 Polymerization

Alkenes undergo polymerization to form several useful polymers. Polymers are molecules with high molecular masses. Many molecules of monomer add together to form one large molecule of polymer.



The polymer formed is named polyethene or polythene.

Polymers are very helpful in our day-to-day life. Plastics, synthetic fibres, *etc.*, are examples of polymers.

Some methods of preparation of alkenes and their typical reactions are summarized in Table 17.4. Table 17.5 includes the common polymers.

17.10. PROPERTIES AND REACTIONS OF ALKYNES

Physical properties follow the pattern of those of alkanes and alkenes.

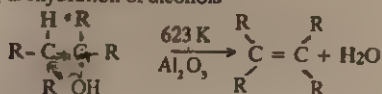
Table 17.4

Preparation of alkenes

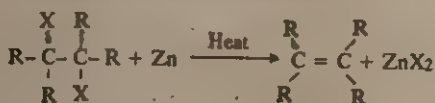
1. Dehydrohalogenation of haloalkanes



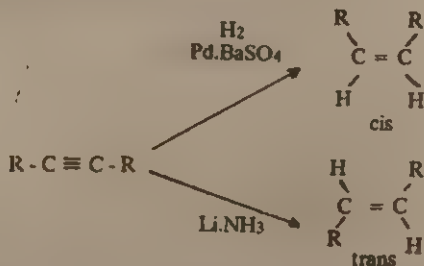
2. Dehydration of alcohols



3. Dehalogenation of vicinal dihalides

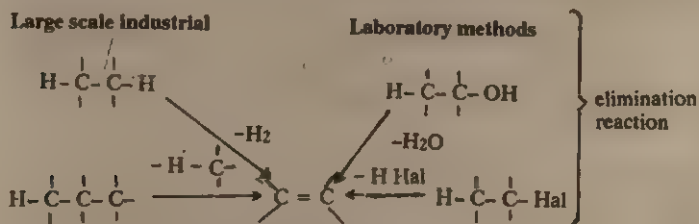


Reduction of alkynes



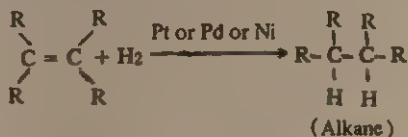
Important alkene synthesizing reactions.

All are elimination reactions and the molecules eliminated are shown over the arrows.

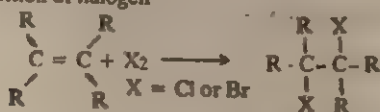


Reactions of Alkenes

1. Addition of hydrogen

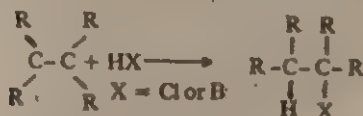


2. Addition of halogen



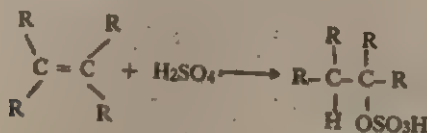
Dihaloalkane

3. Addition of hydrogen halide,



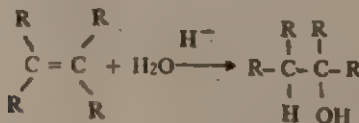
Haloalkane

4. Addition of sulphuric acid



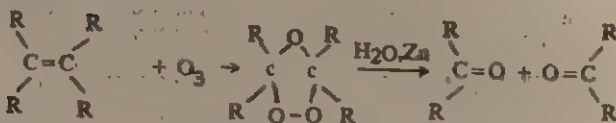
alkylhydrogensulphate

5. Addition of water



alcohol

6. Ozonolysis



an ozonide

7. Hydroxylation

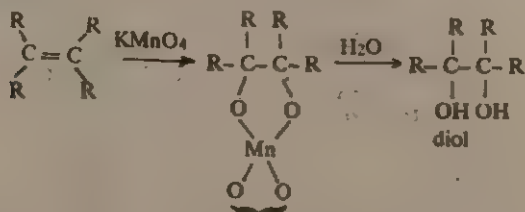
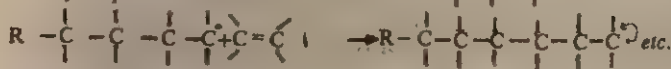
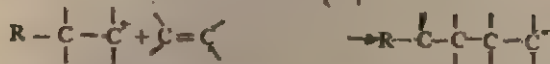


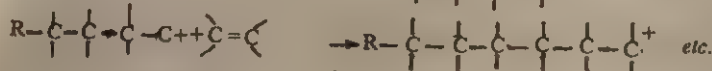
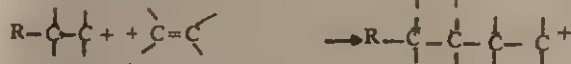
Table 17.4 contd.....

8. Polymerization.

(a) Radical initiation



(b) Cation initiation



(c) anion polymerization

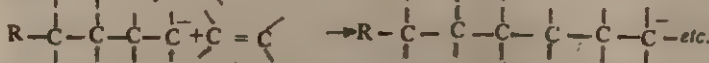
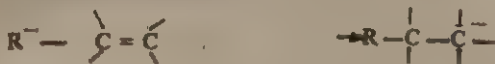
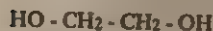


Table 17.5

(1) Addition polymers

Monomer	polymer
$CH_2 = CH_2$ Ethene	$\{CH_2 - CH_2\}_n$ Polyethene (polyethylene)
$CH_2 = CHCl$ Chloroethene	$\{CH_2 - \underset{ }{CH}\}_n$ polychloroethene (polyvinyl chloride)
$CH_2 = CHPh$ Phenylethene	$\{CH_2 - \underset{ }{CH}\}_n$ polyphenylethene (polystyrene) Ph
$CH_2 = CHOAc$ Ethanoxyethene	$\{CH - \underset{ }{CH}\}_n$ polyethanoxyethene (polyvinyl acetate) OAc
$CH_2 = CF_2$ Tetrafluoroethene:	$\{CF_2 - CF_2\}_n$ Teflon
$CH_2 = CHCN$ Cyanoethene	$\{CH_2 - \underset{ }{CH}\}_n$ Orlon CN
$CH_2 = \underset{ }{C}(\overset{CH_3}{ }) - CH - CH_2$ 2-methyl-1,3-butadiene (Isoprene)	$\{CH_2 - \underset{ }{C}(\overset{CH_3}{ }) = CH - CH_2\}_n$ Natural rubber

(2) Condensation polymers



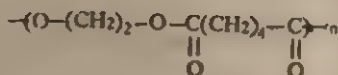
1,2-Ethanediol

(ethylene glycol)

+



Hexanedioic acid

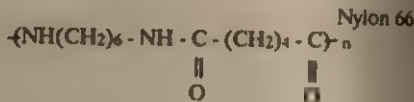


Dacron



1,6-diaminohexane

(Hexamethylenediamine)



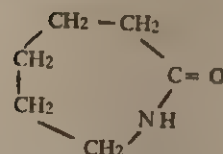
Nylon 66

+



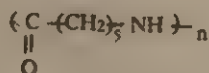
Hexanedioic acid

(Adipic acid)



Azacycloheptan-2-one

(γ -caprolactam)



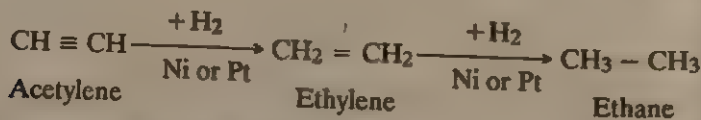
Nylon 6

Alkynes contain a carbon-carbon triple bond which is made of a strong σ bond and two weak π bonds. The alkynes readily undergo additional reactions, the majority of which involve electrophilic addition. The important reactions of alkynes are discussed below.

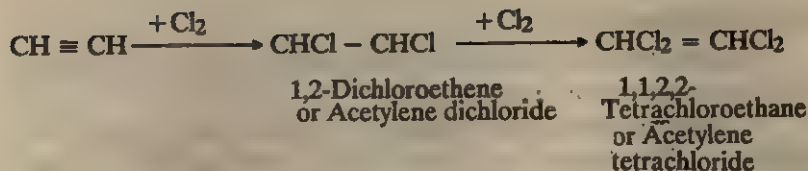
17.10.1 Electrophilic Addition Reactions

Like alkenes, alkynes also form addition products.

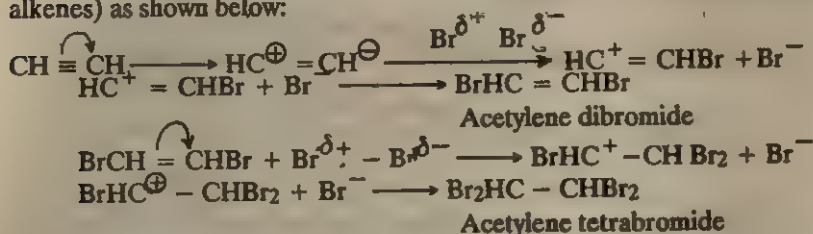
(i) **Addition of hydrogen** : Hydrogen, in presence of a suitable catalyst, attack the $-\text{C} \equiv \text{C}-$ triple bond to give saturated hydrocarbons.



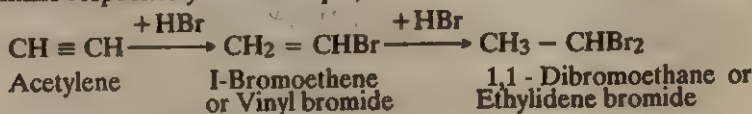
(ii) **Addition of halogens** : Chlorine and bromine attack alkynes to form di- and tetrahalides. For example,



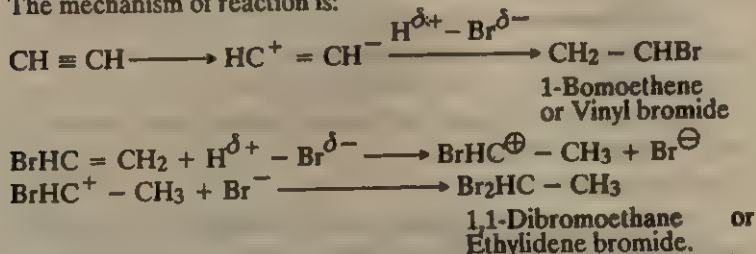
The mechanism involved is of electrophilic type (as in the case of alkenes) as shown below:



(iii) Addition of halogen acids : Acids add on to alkynes according to Markovnikov's rule yielding mono and dihalogen derivatives of alkene and alkane respectively. For example,



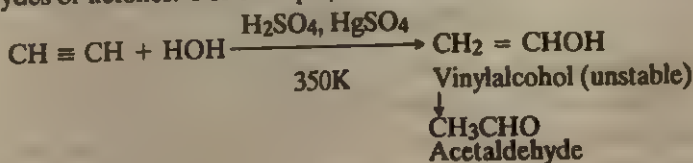
The mechanism of reaction is:



Chloroethene is the monomer from which polychloroethene, the important plastic known as polyvinyl chloride or PVC, is obtained.



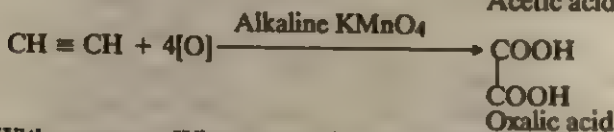
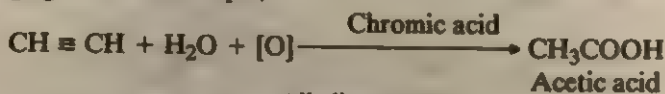
(iv) Addition of water : Water, in presence of dilute H_2SO_4 and mercuric sulphate, adds on to alkynes forming carbonyl compounds, aldehydes or ketones. For example,



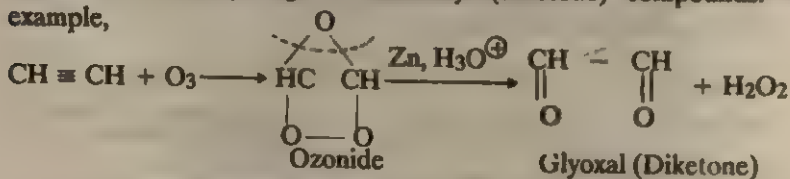
17.10.2 Oxidation of alkynes

Alkynes are readily oxidized forming different products depending upon the nature of oxidizing agent used.

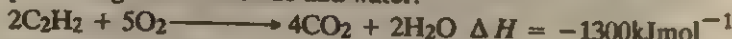
(i) **With potassium permanganate** : Alkynes on oxidation with potassium permanganate or chromic acid yield carboxylic acids. However, the nature of acids obtained may be different in the case of two oxidizing agents. For example,



(ii) **With ozone** : When ozone is passed through a solution of alkynes in an inert solvent, the latter gets oxidized forming ozonide. The ozonide on hydrolysis gives dicarbonyl (diketone) compounds. For example,



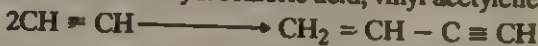
(ii) **Combustion** : Alkynes burn in air or oxygen with a luminous flame producing carbon dioxide and water.



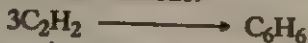
The reaction is "highly exothermic" yielding approximately 1248 kJ mol⁻¹ of energy (heat).

17.10.3 Polymerization

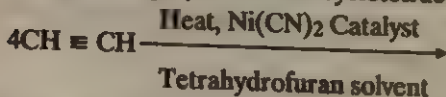
When acetylene is passed through a solution of cuprous chloride and ammonium chloride in hydrochloric acid, vinyl acetylene is formed.



When acetylene is passed through a red hot copper tube three molecules join together to form benzene.



Acetylene is polymerized to cyclotetraene

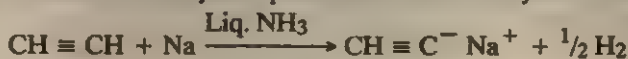


Formation of Acetylides

Alkynes react with alkali metals in the presence of liq. NH₃ and form salts known as acetylides. The acetylenic hydrogen of terminal alkynes is removed as a proton by the strong base. The

Cyclotetraene

amide ion, being the anion of very weak acid ammonia, is strong and is able to remove the acetylenic protons of terminal alkynes. For example,



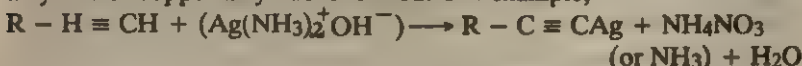
Sodamide

Sodium acetylide

Sodium acetylides (or alkynides) are useful intermediates for the preparation of other alkynes. This is accomplished by treating the sodium alkynide with a primary alkyl halide.

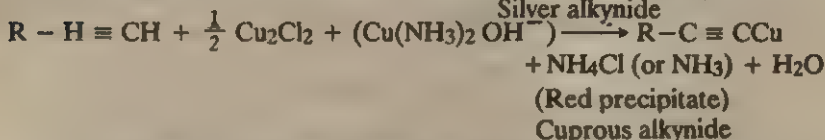


(2) When alkynes are passed through ammoniacal solutions of silver nitrate or copper sulphate, a characteristic precipitate of silver alkynide or copper alkynide is formed. For example,



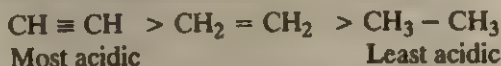
(White precipitate)

Silver alkynide



The formation of these characteristic coloured acetylides can be used for distinguishing terminal alkynes ($\text{R} - \text{C} \equiv \text{CH}$) from other hydrocarbons. Non-terminal alkynes do not give a precipitate. Silver alkynes are soluble in nitric acid, whereas silver halides are not.

These reactions are given only by alkynes. These reactions could be possible because of their acidic nature. Carbon atom in these hydrocarbons assume sp hybridization which bears more character compared to sp^2 and sp^3 orbitals. An electron in an s orbital is tightly held by the nucleus which supports its strong electronegative character. Because of this, the hydrogen of acetylenic carbon develops a more positive charge and is, thus, acidic in character. The acidic character of hydrocarbons decreases the order.



Important methods for the preparation of alkynes and their reactions are summarized in Table 17.6.

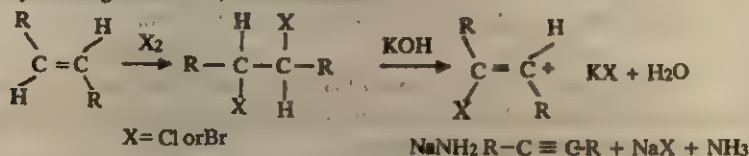
17.11. REACTIONS OF ARENES (AROMATIC HYDROCARBONS)

Aromatic hydrocarbons are unsaturated cyclic compounds. They are also known as arenes. They are highly unreactive towards chemical reagents because of conjugated unsaturated ring system present in them.

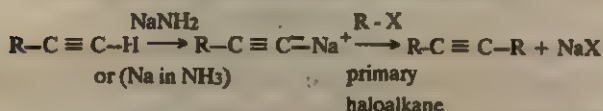
Table 17.6

Preparation of alkynes

Dehydrohalogenation of 1,2-dihaloalkanes

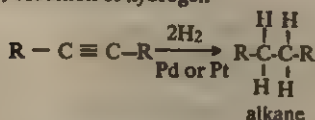


Reaction of sodium acetylides with primary haloalkanes

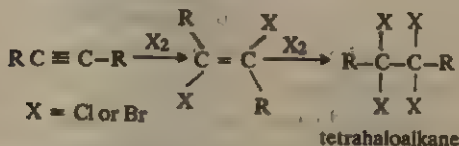


Reactions of alkynes

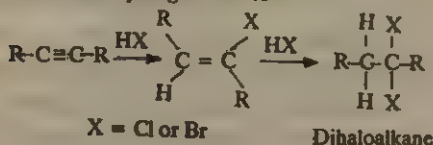
1. Addition of hydrogen



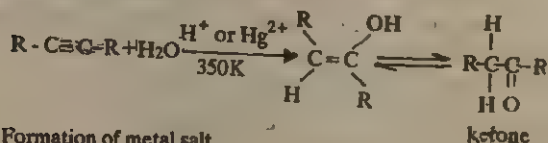
2. Addition of halogens



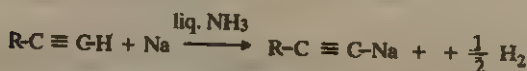
3. Addition of hydrogen halides



4. Addition of water



5. Formation of metal salt



They do not easily undergo addition reactions. Under drastic conditions, such as high temperatures, presence of a catalyst, *etc.*, hydrocarbons undergo substitution reactions in preference to addition reactions. The hydrogen atoms of benzene and its homologues can be replaced by nitro ($-\text{NO}_2$), halogen ($-\text{X}$), sulphonic acid group ($-\text{SO}_3\text{H}$) *etc.* Some addition reactions are also possible under highly specific and drastic conditions – increased concentration, high temperatures and pressures and presence of catalysts.

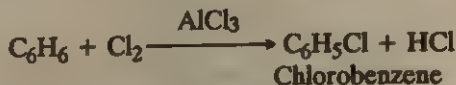
Benzene and its homologues are versatile solvents. They dissolve a large number of compounds. This is because the electron cloud makes it polar to some extent, and therefore, even polar molecules are attracted towards it. Nucleophilic species such as Cl^- , OH^- , CN^- *etc.*, do not attack the benzene ring as they are repelled by the delocalized π electron cloud. However, electrophiles such as H^+ , Cl^+ , NO_2^+ *etc.*, can attack the benzene ring and for this reason benzene ring and for this reason benzene and its homologues undergo electrophilic reactions.

Some of the important reactions of arenes are discussed in the following pages by considering benzene as a typical example of the aromatic compounds.

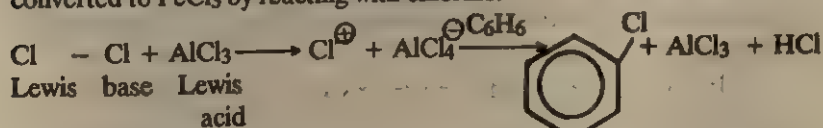
17.11.1 Electrophilic substitution reactions

The hydrogen atoms present in benzene ring can readily be replaced by other atoms or groups when electrophilic reagents attack on it.

(i) **Halogenation** : Benzene undergoes a substitution reaction with chlorine or bromine in the presence of a halogen carrier, like anhydrous AlCl_3 or FeCl_3 .



In this reaction, iron can also be used as a catalyst, since it gets converted to FeCl_3 by reacting with chlorine.

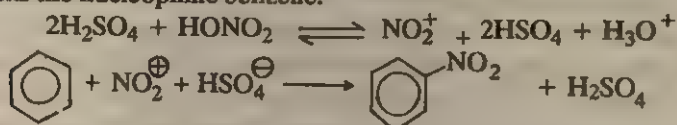


Direct iodination takes place in presence of oxidizing agents like iodic acid or nitric acid.

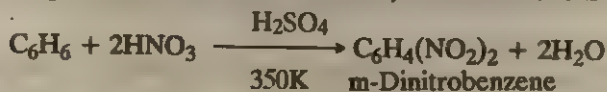


(ii) **Nitration** : When benzene is nitrated with a mixture of HNO_3 and conc. H_2SO_4 at about 330K, nitrobenzene is obtained. The nitrating

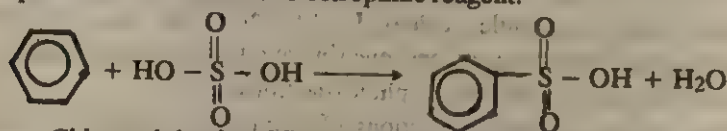
mixture generates the electrophilic reagent, nitronium ion, NO_2^+ which attacks the nucleophilic benzene.



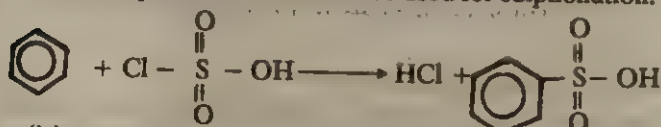
If a temperature of about 350K is used, dinitrobenzene is obtained.



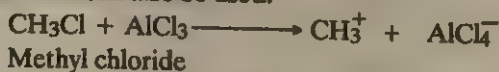
(iii) **Sulphonation** : Sulphonation of benzene takes place when it is heated with fuming sulphuric acid (concentrated $\text{H}_2\text{SO}_4 + \text{SO}_3$). Sulphur trioxide acts as an electrophilic reagent.



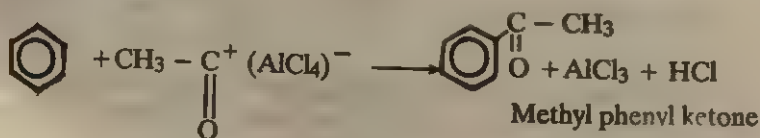
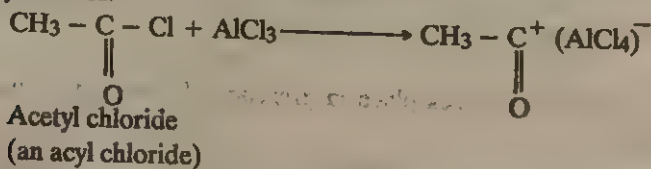
Chlorosulphonic acid can also be used for sulphonation.



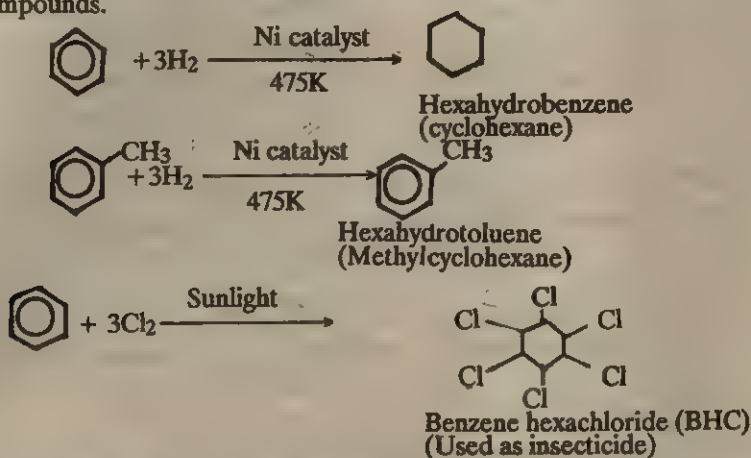
(iv) **Friedel - Crafts reaction** : Alkyl substituted benzenes are obtained by the reaction of benzene with alkyl halides in the presence of Lewis acid, anhydrous AlCl_3 . The other Lewis acid catalyst like FeCl_3 , BF_3 and HF can also be used.



The reaction (known as Friedel-Crafts Reaction) can also be used to prepare mixed aromatic aliphatic ketones by taking acyl halides instead of alkyl halides.

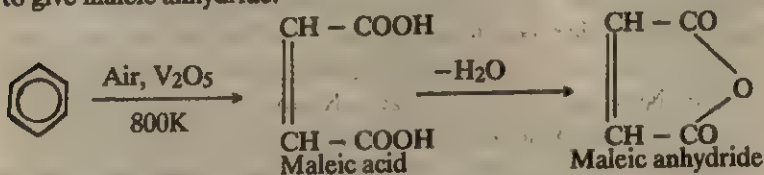


Benzene and its homologues undergo some addition reactions similar to alkenes and alkynes but under some severe conditions. For example, benzene (or toluene) can add up hydrogen (in the presence of nickel catalyst at 475K) or chlorine (in presence of sunlight) to give saturated compounds.

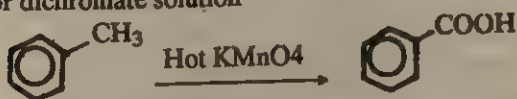


17.11.3 Oxidation and Combustion

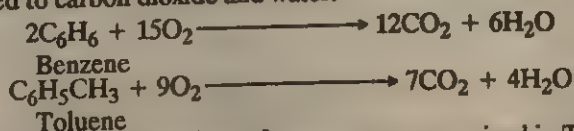
Benzene can be oxidized with air at 800K in the presence of V_2O_5 catalyst to give maleic anhydride.



Toluene is oxidized to benzoic acid with potassium permanganate or dichromate solution



On burning in air, benzene and toluene produce a smoky flame and are oxidized to carbon dioxide and water.

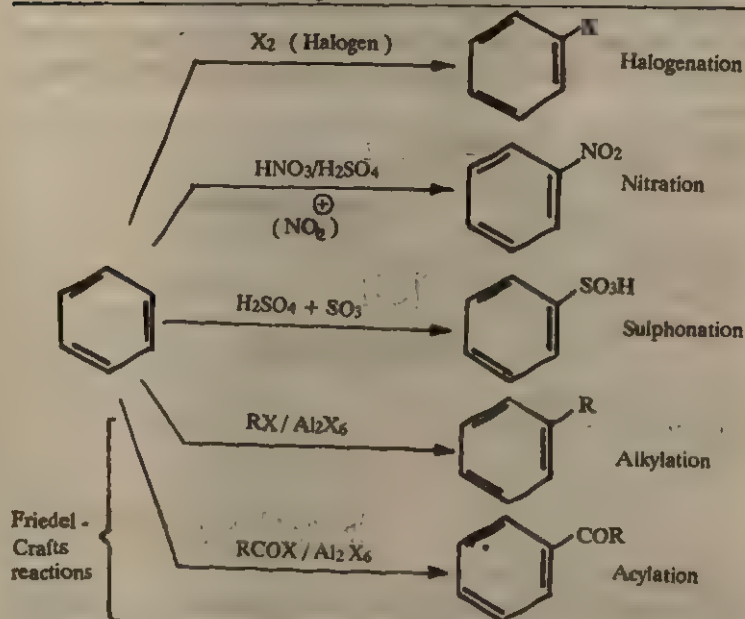


Important substitution reactions of arenes are summarized in Table 17.7

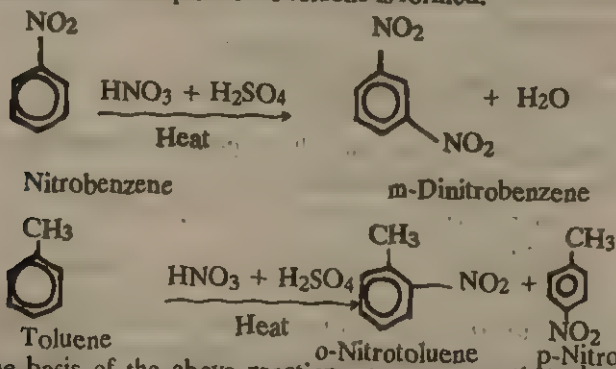
17.12 ORIENTATION IN ELECTROPHILIC SUBSTITUTION

The six hydrogen atoms of benzene molecule are equivalent. The replacement of any one hydrogen atom of benzene ring by another group does not lead to any isomeric products. However, the replacement of

TABLE 17.7. Important substitution reactions of arenes



second hydrogen atom leads to isomeric disubstituted products. These disubstituted isomeric products are ortho (1:2); meta (1:3) and para (1:4). It has been found that the type of disubstitution products formed depends on the nature of the group already present in the ring. Thus, if nitrobenzene is further nitrated the second nitro group will occupy the meta position of the ring. On the other hand, when toluene is nitrated a mixture of ortho and para nitro toluene is formed.



On the basis of the above reactions, one can say that nitro group has m-directing whereas methyl group has ortho and para directing nature. Thus, the group already present in the nucleus of benzene has a directive or orienting influence on the position of the new substituent in the benzene ring.

On the basis of their directive influence the groups present in mono substituted benzene ring are classified as ortho and para directing or meta directing groups as given below:

(i) **Ortho-para directing groups** are $-\text{CH}_3$ (methyl); $-\text{C}_2\text{H}_5$ (ethyl); $-\text{OH}$ (hydroxy); $-\text{NH}_2$ (amino); $-\text{Cl}$ (chloro); $-\text{Br}$ (Bromo) and $-\text{I}$ (Iodo)

(ii) **Meta directing groups** are $-\text{NO}_2$ (nitro); SO_2OH (sulphonic);

$-\text{CN}$ (cyanide); $-\text{CHO}$ (aldehydic); $-\text{COR}$ (ketonic); $-\text{COOH}$ (carboxylic).

A number of empirical rules have been formulated to predict the position of new entrant in the benzene nucleus. Of these Crum Brown and Gibson rule is very satisfactory. According to it "if a substituent X, already present in the nucleus, is such that its hydrogen compound, H X can be easily oxidized to its hydroxy compounds (HOX), it directs the new entering group to the meta position, otherwise in the ortho and para HCHO , which can be easily oxidized to HCOOH , hence, $-\text{CHO}$ group is meta directing. Similarly, NO_2 group with hydrogen forms HNO_2 which is readily oxidized to HNO_3 , hence $-\text{NO}_2$ is also meta directing. On the other hand $-\text{NH}_2$ group forms NH_3 , which cannot be easily oxidized, so $-\text{NH}_2$ group is ortho and para directing. Other groups with their directive influence are given in Table 17.8.

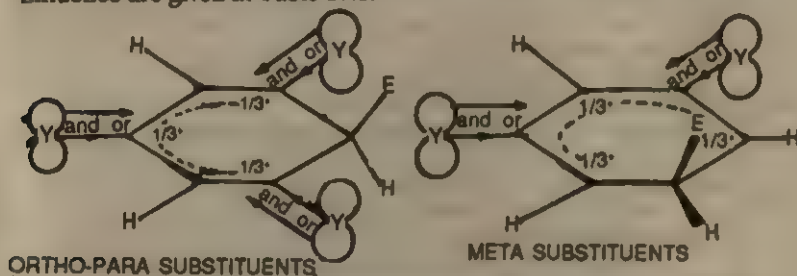


Diagram showing how electrons releasing substituents stabilize the Wheland intermediate for ortho-para substitution as compared with meta substitution

TABLE 17.8 Directive Influence Of Groups

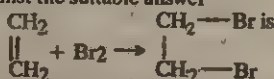
Name of the group	Formula	Directive influence
Nitro	$-\text{NO}_2$	meta
Aldehydic	$-\text{CHO}$	meta
Ketonic	O \parallel $-\text{C}-\text{R}$	meta
Carboxylic	$-\text{COOH}$	meta
Methyl	$-\text{CH}_3$	ortho and para
Ethyl	$-\text{C}_2\text{H}_5$	ortho and para
Amino	$-\text{NH}_2$	ortho and para
Halogen(chloro-bromo and iodo)	$-\text{X}(-\text{Cl}, -\text{Br}, -\text{I})$	ortho and para

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

17.1 Put a tick (✓) mark against the suitable answer

(i) The reaction :



- (a) a substitution reaction (b) an addition reaction
(c) a condensation reaction (d) none
- (ii) The main source of most organic compounds is
(a) coal gas (b) coal gas and petroleum
(c) methane (d) petroleum
- (iii) Photochemical chlorination of alkane is initiated by a process of
(a) homolysis (b) pyrolysis (c) substitution
(d) peroxidation
- (iv) When petroleum is heated gradually first batch of vapours evolved will be rich in
(a) kerosene oil (b) diesel (c) petroleum ether
(d) lubricating oil
- (v) Ethylene from ethyl bromide is obtained by treating it with
(a) hydrogen (b) alcoholic caustic potash
(c) aqueous caustic potash (d) aqueous caustic soda.
- (vi) Most of the hydrocarbons from petroleum are obtained by
(a) fractional crystallization (b) pyrolysis (c) cracking (d) fraction distillation
- (vii) When acetylene is passed through dilute H_2SO_4 in presence of HgSO_4 , the compound formed is
(a) ethanol (b) acetone (c) carbide Hg (d) acetaldehyde.
- (viii) When acetylene is reacted with HBr , we get,
(a) methyl bromide (b) ethyl bromide (c) ethylene bromide (d) ethylidene bromide
- (ix) The final product on the oxidation of hydrocarbon is
(a) acid (b) aldehyde (c) dihydric alcohol (d) $\text{H}_2\text{O} + \text{CO}_2$
- (x) Aromatic character is possible only when
(a) six electrons are delocalised (b) the molecule is cyclic and planar (c) the molecules has six atoms in a ring (d) a molecule has at least two reaonance structures.

17.2 Fill in the blanks :

- (i) The various products are obtained from the petroleum by the process of _____.
- (ii) Both coal and petroleum are known as _____.
- (iii) The process of splitting of high molar mass alkanes into smaller fragments by heat is called _____.
- (iv) The internal combustion engine makes a metallic sound _____.
- (v) The best fuels for resistance to knocking are _____ such as _____.
- (vi) _____ are converted to aromatic hydrocarbons by the process called _____.
- (vii) Alkenes and alkynes are called _____ hydrocarbons because the double and triple bond can open to react with chemical reagents.
- (viii) Electrophilic reagents are _____ in nature.

(ix) The _____ rule states that in addition of a compound HX to an unsaturated compound, hydrogen becomes attached to the unsaturated carbon.

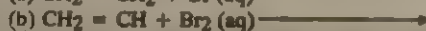
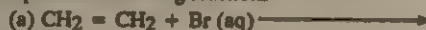
(x) A polymer of ethylene is called _____.

17.3 Mark the True (T)/False (F) statements of the followings.

- (i) Petroleum is heavier than water and soluble in it.
- (ii) Aromatic hydrocarbons are obtained by fractional distillation.
- (iii) Alkyl magnesium halides are known as Grignard reagents.
- (iv) Decarboxylation involves the removal of carbon from a hydrocarbon.
- (v) Calcium carbide on reacting with water gives hydrogen.
- (vi) The boiling points of alkanes increase with increase in their molecular mass.
- (vii) Benzene is a poor solvent.
- (viii) The delocalization of electrons in the benzene ring attributes to its stability.
- (ix) Acetylene is acidic in nature.
- (x) Vinyl chloride is also called chloroethene.

SHORT ANSWER QUESTIONS

17.4 (I) Complete the following reactions



(ii) Why does ethylene decolourize bromine water, while ethane does not do so ?

(iii) Give one example each of:

(i) an addition reaction of chlorine

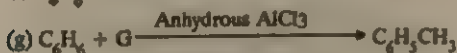
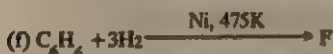
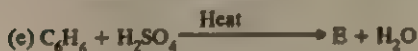
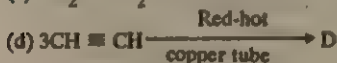
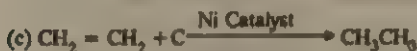
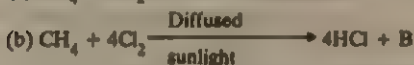
(ii) a substitution reaction of chlorine

(iv) (a) Name the products obtained by the combustion of saturated and unsaturated hydrocarbons.

(b) Ethane burns in oxygen to form carbon dioxide and water. Write balanced chemical equation for this reaction.

(v) What do you understand by unsaturation. How will you test unsaturation in an organic compound.

(vi) Provide the missing details in the following equations.



TERMINAL QUESTIONS

- 17.1 What is meant by homolytic and heterolytic fission ? Explain with examples the formation of free radicals, carbonium ions and carbanions.
- 17.2 What are electrophilic and nucleophilic reagents ? Which of the two, would readily attack a carbonium ion and why ?
- 17.3 Define and give examples of the following reactions.
 (i) addition reaction (ii) substitution reaction
 (iii) elimination reaction (iv) rearrangement reaction
- 17.4 What is Markovnikov's rule ? How will you justify it on theoretical basis ?
- 17.5 Describe the chemical properties of alkynes with reference to :
 (i) addition of hydrogen (ii) addition of halogens
 (iii) addition of halogen acids (iv) oxidation
- 17.6 Describe in detail the electrophilic substitution reactions of arenes.
- 17.7 Comment on the followings
 (i) Why are the boiling points of branched chain alkanes lower than their normal isomers ?
 (ii) Why do alkanes containing odd number of carbon atoms have lower melting points than expected value ?
 (iii) Why do the boiling points of alkenes increase from 1-propene to 1-heptene ?
- 17.8 What is the directive influence of
 (i) an electron-releasing group (ii) an electron-withdrawing group?
- 17.9 (a) In an electrophilic substitution why does OH group direct the newly entering group in ortho or para position ?
 (b) In an electrophilic substitution reaction why does NO₂ group direct the new entering group in the meta position ?
- 17.10 (a) List at least five electrophilic reagents.
 (b) List at least five nucleophilic reagents.
- 17.11 What is Friedel-Crafts reaction ? Give suitable examples.
- 17.12 How would you distinguish methane, ethylene and acetylene from each other.
- 17.13 Why does benzene not undergo addition reactions in spite of unsaturation.
- 17.14 Explain by writing suitable equations what happens when:
 (a) Propane is treated with HBr.
 (b) Ethene is heated with hydrogen in the presence of a nickel catalyst.
 (c) Ethane is treated with concentrated sulphuric acid containing some mercuric sulphate.
 (d) Acetylene is bubbled through 40% sulphuric acid containing some mercuric sulphate.
 (e) Ethene is treated with cold, dilute alkaline potassium permanganate.
 (f) Acetylene is passed through Tollen's reagent.
 (g) Toluene is treated with hot, alkaline potassium permanganate
 (h) Benzene is heated with methyl chloride in the presence of anhydrous aluminium chloride.

ANSWERS TO SELF ASSESSMENT QUESTIONS

- 17.1. (i) b (ii) d (iii) d (iv) c (v) b (vi) d (vii) d (viii) d (ix) d (x) b
- 17.2 (i) fractional distillation (ii) fossil fuels (iii) cracking (iv) knocking
 (v) branched chain hydrocarbons 2,2,4-trimethylpentane
 (vi) straight chain alkanes, reforming (vii) unsaturated, (viii) electron deficient
 (ix) Markovnikov's (x) polythene
- 17.3 (i) F, (ii) T, (iii) T, (iv) F, (v) F, (vi) T, (vii) F,
 (viii) T, (ix) T, (x) T.

- 17.4 (i) (a) $\longrightarrow \text{CH}_2\text{Br} - \text{CHBr}$
 1,2-Dibromomethane or Ethylene dibromide
 (b) $\longrightarrow \text{CHBr}_2 = \text{CHBr}$
 1,2-Dibromoethene or Acetylene dibromide
 $\longrightarrow \text{CHBr}_2 - \text{CHBr}_2$
 Acetylene tetrabromide
- (ii) Ethylene is an unsaturated hydrocarbon and forms addition compound with bromine water, Ethane is a saturated hydrocarbon and does not react with bromine water.
- (iii) (i) $\text{CH}_2 = \text{CH}_2 + \text{Cl}_2 \longrightarrow \text{CH}_2\text{ClCH}_2\text{Cl}$
 Ethylene Ethylene dichloride
 (ii) $\text{CH}_4 + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \text{HCl}$
 Methane Methyl chloride
 $\text{CH}_3\text{Cl} + \text{Cl}_2 \longrightarrow \text{CH}_2\text{Cl}_2 + \text{HCl}$
 Dichloromethane
 $\text{CH}_2\text{Cl}_2 + \text{Cl}_2 \longrightarrow \text{CHCl}_3 + \text{HCl}$
 Trichloromethane
 $\text{CHCl}_3 + \text{Cl}_2 \longrightarrow \text{CCl}_4 + \text{HCl}$
 Carbon tetrachloride
- (iv) (a) CO_2 and H_2O
 (b) $2\text{CH}_3\text{CH}_3 + 7\text{O}_2 \longrightarrow 4\text{CO}_2 + 6\text{H}_2\text{O}$
- (v) Organic compounds in which there is at least one double or triple bond in carbon chain are called unsaturated compounds. In such compounds carbon atoms combine with another carbon through two or three pairs of electrons. An unsaturated compound is reactive particularly for addition reactions. Such a property of unsaturated compounds is called unsaturation..
 Bromine water is instantly decolourized by unsaturated compounds due to addition reactions. Now, if on adding a few drops of aqueous bromine to the organic compound, the brown colour of bromine is discharged, then the compound is unsaturated.
- (vi) (a) A = C (b) B = CCl_4 (c) C = H_2 (d) C_6H_6
 (e) E = $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ (f) F = C_6H_{12} (g) G = CH_3Cl (h) H = $\text{C}_6\text{H}_5\text{COOH}$

Purification and Characterization of Organic Compounds

Someone who had begun to read geometry with Euclid, when he had learned the first proposition, asked Euclid, "But what shall I get by learning these things?" Whereupon Euclid called his slave and said, "Give him three-pence since he must make gain out of what he learns".

STOBAEUS
(Circa 500 A.D.)

UNIT PREVIEW

18.1 Introduction

18.2 Purification : crystallization, sublimation, distillation, extraction and chromatography

18.3 Qualitative analysis of elements : carbon, hydrogen, nitrogen, halogens, etc.

18.4 Quantitative analysis of elements : estimation of carbon, hydrogen, nitrogen, halogen, etc.

18.5 Determination of molecular mass : Victor Meyer's method, elevation of boiling point and depression of freezing point method and volumetric method

18.6 Calculation of empirical and molecular formulae

18.7 Modern methods of structure elucidation

Self assessment questions

Terminal questions

Answers to self assessment questions

LEARNING OBJECTIVES

At the completion of this unit, you should be able to:

1. Describe the principles involved in the different methods of purification : filtration, crystallization, sublimation, distillation, fractional distillation, extraction and chromatography.
2. Apply the above techniques/processes for the purification of some simple mixtures.
3. Describe the chemical reactions involved in the qualitative analysis of organic compounds using the sodium fusion test.
4. Describe and explain the principles involved in the different methods of quantitative estimation of carbon, hydrogen, nitrogen, etc. in organic compounds.
6. Calculate the empirical and molecular formulae of organic compounds.
7. Comment on the modern methods of structure elucidation.

18.1 INTRODUCTION

A substance used in chemistry should be pure. If not, we get wrong ideas about it. In daily life pure has a different meaning. We buy pure honey. We eat pure butter. We wear clothes made of pure wool. Honey, butter and wool are mixtures. In science pure has only one meaning. A pure substance is a single substance. Definite physical and chemical properties and colour and shape of the crystals of a substance are attributed to its purity. The nature of the substance to be purified determines the method of purification. Once the compound is purified, one can proceed to investigate its compositions etc. The different steps after purification employed in the characterization of organic compounds are: (a) qualitative analysis, (b) quantitative analysis, (c)

molecular mass determination, (d) calculation of the empirical and molecular formulae, and (e) determination of structure by one or more of several methods including chemical methods. In this unit, we shall deal with some of methods commonly employed for the purification and characterization of organic compounds.

18.2 PURIFICATION

The nature of the organic substances to be purified determines the method of purification to be employed. The common techniques used are: (i) crystallization, (ii) sublimation, (iii) distillation, (iv) differential extraction, and (v) chromatography.

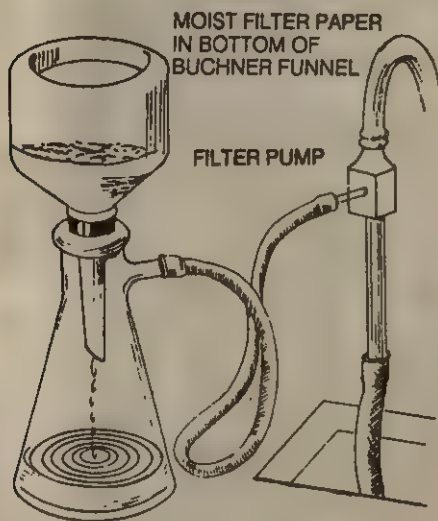


Fig. 18.1. Use of Buchner funnel

18.2.1 Filtration

This process is usually employed for the separation of insoluble solid impurities from a soluble substance. Quick filtration may be effected with the help of a buchner funnel and a pump (Fig. 18.1).

18.2.2. Crystallization

This technique is used for separating or purifying a solid substance which is soluble in solvents like water, alcohol, ether, benzene, chloroform, carbon tetrachloride, acetone, etc. The efficiency of the

process depends upon the choice of suitable solvents. A good solvent is one which dissolves a large amount of the substance at an elevated temperature and from which crystals separate out on cooling. Since most of the solvents are highly inflammable their use require a careful handling.

Procedure : A hot saturated solution of the substance in a solvent is filtered hot. Undissolved impurities are left on the filter bed. Funnel surrounded with hot water jacket is employed to prevent crystallization during the course of filtration. The filtered solution is allowed to cool slowly. After some time crystals start appearing. The crystals are then separated by filtration and dried in a vacuum desiccator.

A mixture of common salt and sugar is separated by dissolving the mixture of ethanol. Sugar dissolves while common salt remains insoluble. Similarly a mixture of naphthalene and benzoic acid can be separated by taking the mixture in hot water. Benzoic acid dissolves and naphthalene remains undissolved.

18.2.3 Fractional Crystallization

In case the compound and the impurities do not differ much in their solubilities, then separation can be effected by fractional crystallization. On cooling the hot saturated solution, the least soluble component separates out first leaving behind liquor which will be rich in more soluble components. Thus, the first crop of crystals will be richer in the least soluble component, whereas the last one will be richer in highly soluble component present. A number of such repetition will give a pure sample of the compound.

18.2.4 Sublimation

Large number of organic substances such as camphor, naphthalene, anthracene, indigo, anthraquinone, benzoic acid, etc. vapourize directly to gaseous state on heating before they melt and the vapours become solid on cooling. Thus, they can be purified from non-volatile impurities by sublimation technique.

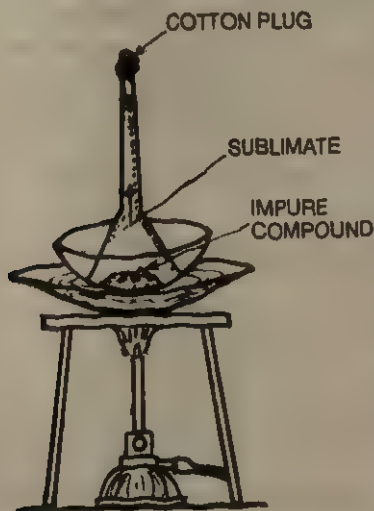


Fig. 18.2. Sublimation

deposited on the inner walls of the funnel. The non-volatile impurities are left behind as residue in the dish. Substances which undergo decomposition when sublimed at ordinary pressure are sublimed under reduced pressure.

18.2.5 Simple Distillation

Purification of a volatile liquid contaminated with non-volatile impurities is done by this technique. The substance is converted to gaseous

state which on cooling condenses. In case the boiling points of components differ considerably, their separation can be effected by a single distillation operation.

The crude sample is taken in a distillation flask fitted with a thermometer, a condenser and a receiver (Fig. 18.3). The distillation flask is heated and when the boiling points of volatile component is reached, the same begins to distil over. The temperature remains steady until this constituent passes over and then the temperature begins to rise until the boil-

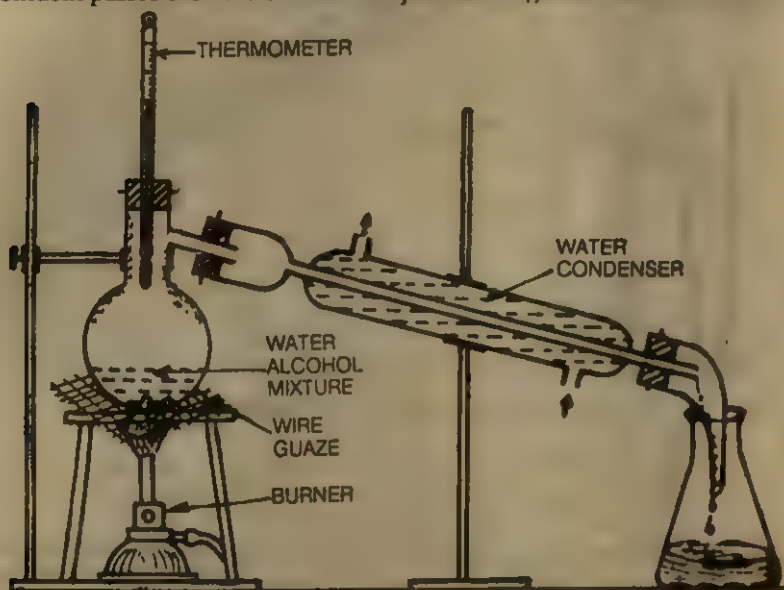


Fig. 18.3. Simple distillation

ing point of next higher boiling component is reached and the same begins to distil over and so on. Bumping and superheating of the liquid is avoided by adding a few small pieces of glass beads of unglazed porcelain or (pumice stone) to the flask.

In a case the boiling point of liquid is above 390K an air condenser (a long wide glass tube attached to the distillation flask) should be employed in place of a Liebig's water condenser. Further purification of the distillate can be achieved by repeating this process until the substance distils over at its boiling point. In case the liquid to be purified is high boiling or decomposes below its boiling point, the distillation is carried out under reduced pressure (Fig. 18.4).

When the boiling points of the liquids are close to each other as in the case of acetone (b.p. 333K) and methyl alcohol (b.p. 338K) they can be separated by fractional distillation (Fig. 18.5) using a fractionating

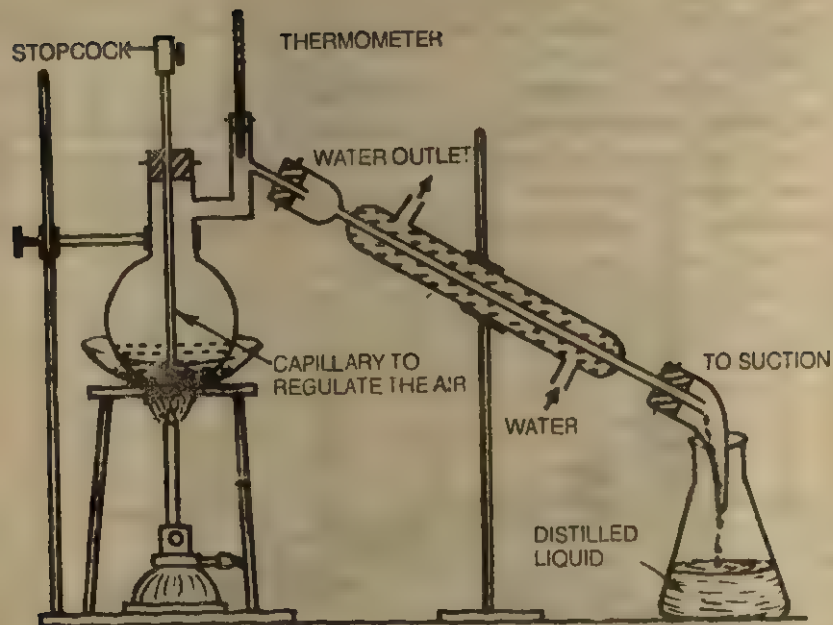


Fig. 18.4 Distillation under reduced pressure

column.

18.2.6 Fractional Distillation

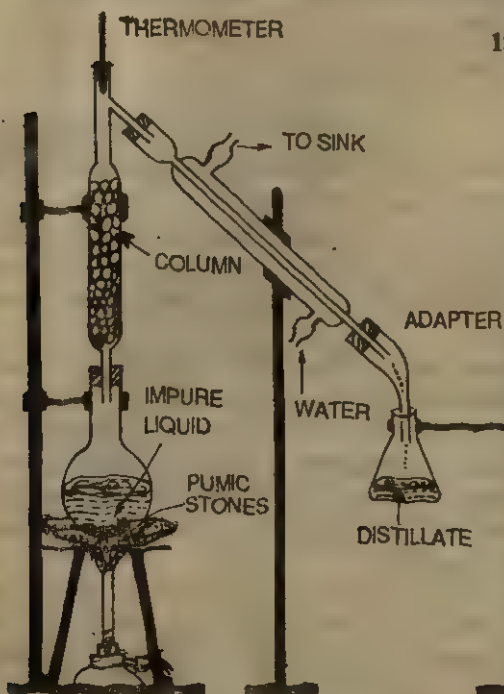


Fig. 18.5 Fractional distillation

There are many types of fractionating columns available (Fig. 18.6) but they fulfil the same purpose, i.e., to increase the cooling surface and to provide an obstruction in the path of ascending vapours and descending liquids. One of the simplest columns consists of a long tube packed with small inert materials such as glass beads (Fig. 18.5) which does not react with the substances being

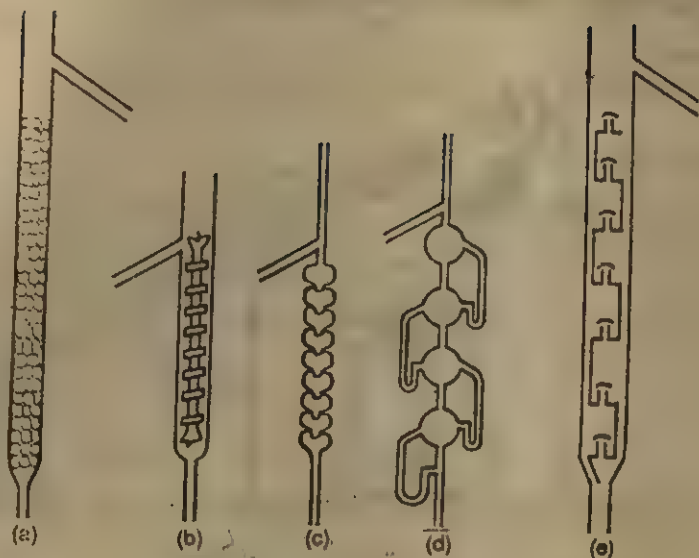


Fig. 18.6. Fractionating columns

distilled. This tube is fitted to the neck of the flask containing the mixture of liquids to be distilled. When a mixture of vapours rises up the column, those of less volatile liquid condense on the glass beads more readily than those of the more volatile liquid. Then as the condensed liquid trickles down the column, it is heated by the rising vapours. Some of it again vapourizes to give vapours richer in the component with the lower boiling point. These vapours condense further up in the column and are heated by the rising vapours. And again the condensed liquid is partially vapourized to give vapours still richer in the lower boiling point component. As a result of the many vapourizations (evaporation) and condensations, the vapours ascending the column become progressively richer in the more volatile liquid, *i.e.*, richer in the lower boiling point liquid. The vapours emerging from the top of a column condense to a liquid which is essentially the pure lower boiling point component, and this is then collected in the receiver. This process is known as fractional distillation.

18.2.7 Steam Distillation

Liquids which are steam volatile and sparingly soluble in water (for example, aniline) may be purified by 'steam distillation' (Fig. 18.7). Steam is passed through the liquid to be purified and the vapours of steam and volatile organic compound are condensed. The distillate is separated into an aqueous layer and an organic compound layer using a

separating funnel (Fig. 18.8). The method is used extensively to purify essential oils and turpentine oil obtained from plants.

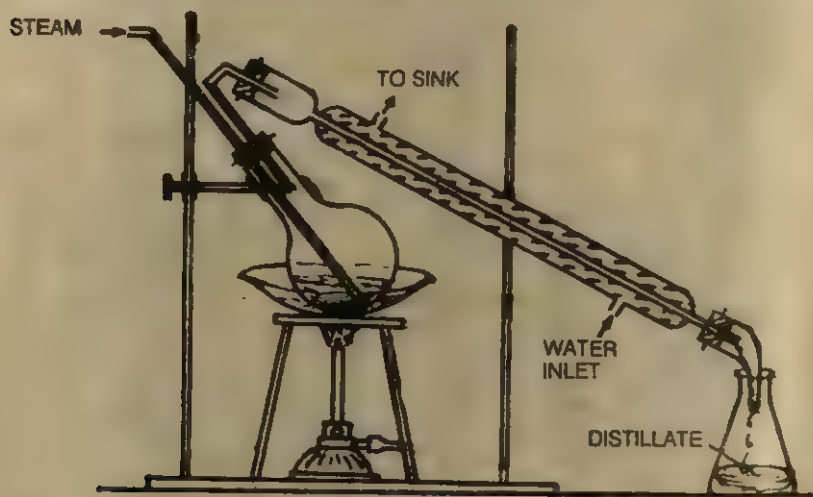


Fig. 18.7. Steam distillation

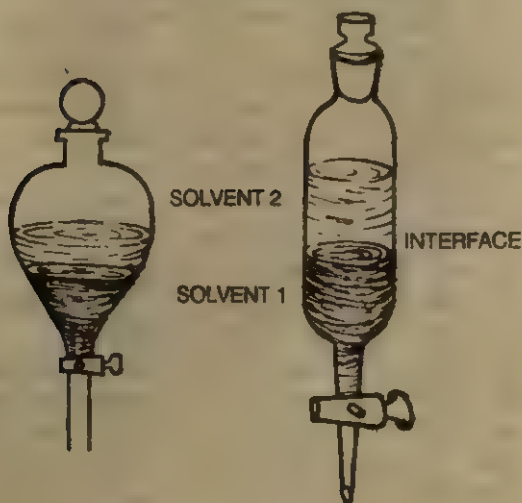


Fig. 18.8. Separating funnels

Theory. Since water and the substance to be separated are immiscible, the sum of their individual vapour pressure, when the mixture boils, must be equal to the atmospheric pressure P (by Dalton's law of partial pressures), i.e.,

$$P = p_L + p_w$$

$$\text{or } p_L = P - p_w$$

Where p_L and p_w are the vapour pressures of the organic compound and water.

Evidently, the partial vapour pressure of each constituent is less than the atmospheric pressure, and hence, the apparent boiling point of each constituent is less than the normal boiling point. Consequently, the principle involved in steam distillation process is somewhat similar to that in vacuum distillation.

Let the masses of the organic substance and water which distils over be W_L and W_w respectively. Let M be the molecular mass of the organic substance. The molecular mass of water, is 18.

$$\frac{W_L}{W_w} = \frac{p_L \times M}{p_w \times 18} = \frac{(P - p_w)M}{p_w \times 18}$$

The value of P and p_w are calculated from the standard tables and barometric height respectively, and hence, the ratio of the masses of organic substance and water in the distillate may be computed.

18.2.8 Differential Extraction

Organic compound, whether solid or liquid, can be recovered from its aqueous solution by shaking it in a separating funnel with a suitable water immiscible solvent in which the organic compound is much more soluble than in water. The separating funnel is then allowed to stand undisturbed for sometime when solvent (containing most of the compound)

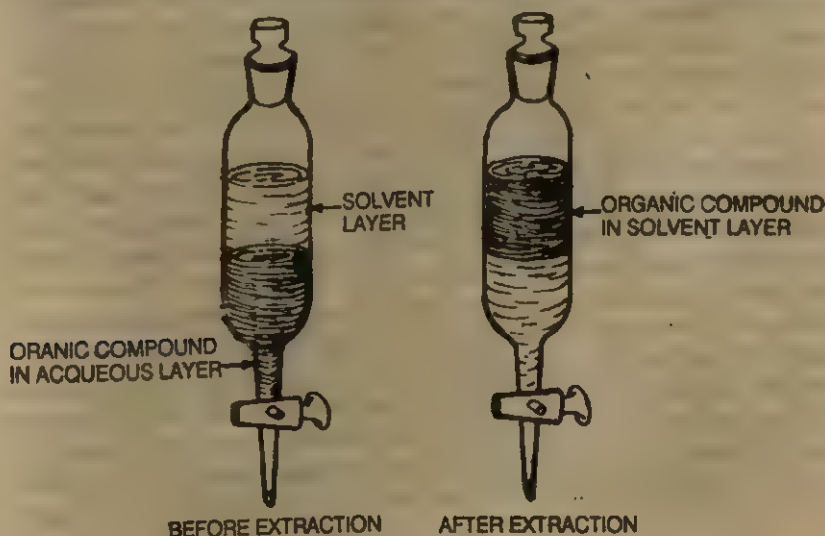


Fig. 18.9. Differential extraction

and water form two separate layers (Fig. 18.9.). The solvent layer is then separated from aqueous layer by opening the tap and washed with water. Now the solvent is removed by distillation when the pure compound is left behind. Benzoic acid, for example, can be purified by its extraction with benzene.

18.2.9 Chromatography

In 1906, the botanist M. Tswett separated a coloured plant pigments (such as chlorophyll) into components of different hues (colours) by passing a solution of the pigment through a column of finely divided adsorptive material such as precipitated chalk (CaCO_3). The method was called chromatography. "Chromatography", as understood today, may be defined as the process of selective retardation of one or more components of a fluid uniformly percolating through capillary passage ways. It is based on the difference in the rate, at which the components of a mixture move through a porous medium (called, the stationary phase) under the influence of some solvent or gas (called, the moving phase).

Chromatography is an extremely valuable method for the separation of ionic and molecular species, non-polar and polar molecules, geometrical and optical isomers, isotopes, *etc.* It has also been used for the identification and purification of the constituents of a mixture. Chromatographic techniques may be classified into (a) column chromatography, (b) paper chromatography, (c) gas chromatography, (d) ion exchange chromatography, *etc.*

The simplest chromatographic method is column chromatography. In this technique, a suitable adsorbent alumina, silica gel, powdered cellulose, finely divided natural silicates or ground glass is packed in a small glass column. The mixture is taken in a suitable solvent. The solution passes through the column; the different components of the mixture get adsorbed at different levels of the column. The components which are adsorbed very strongly are retained at the top while the others are adsorbed at a lower level of the column. If the material consists of only one component, it will show only one adsorption band on the column. This is considered as conclusive test for the purity of the substance. The number of adsorbed bands formed can be detected visually if the components are coloured. Colourless components may be detected spectrophotometrically. The different adsorbed components are then eluted with a selected solvent (mobile phase). The eluent dissolves out the different components from the various adsorbed zones selectively, and thus, 'work out' the different zones (or bands) in the form of solutions which are collected separately. The eluted liquids from each zone is then distilled off to get

MOVING PHASE, e.g.
AN ORGANIC SOLVENT

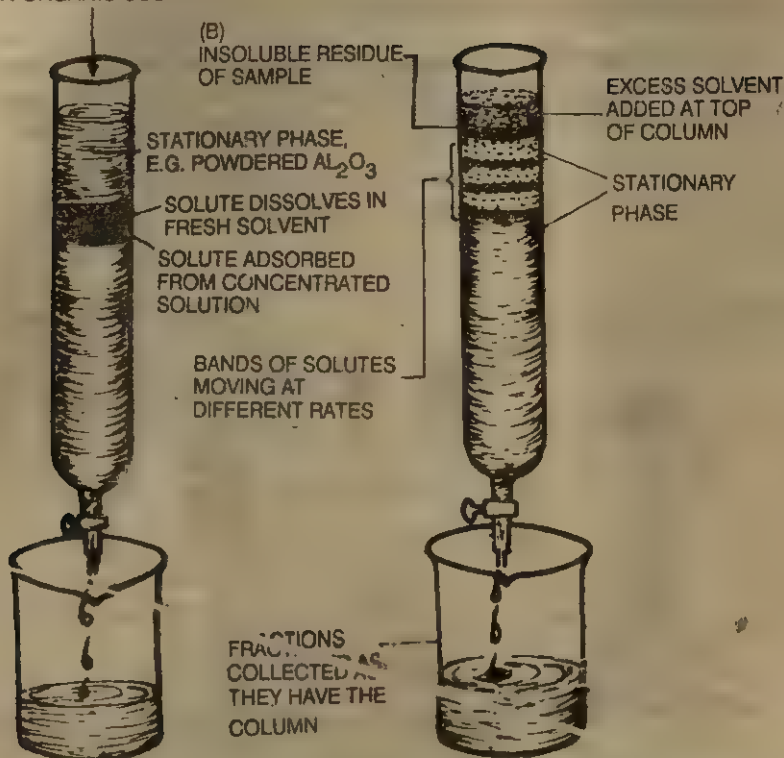


Fig. 18.10. Chromatography: (a) movement of a band of solute through the stationary phase depends on the processes of desorption and readsorption; (b) typical set up for purification by solid-liquid chromatography

the various components in pure form. The eluents usually employed are petroleum ether, carbon tetrachloride, benzene, alcohol, etc. More than one eluent may be used in certain cases. The principle of column chromatography is illustrated in Fig. 18.10.

18.3 QUALITATIVE ANALYSIS OF ELEMENTS

In the study of any organic compound it is necessary to know the elements present in it. The steps to be followed for determining the percentages of elements in the compound are decided on the basis of its elemental analysis.

The elements ordinarily present in organic substances are carbon, hydrogen, oxygen, nitrogen, sulphur and halogens. Their presence can be tested by the tests detailed below.

18.3.1 Tests for Carbon and Hydrogen

A dried sample of the organic substance is mixed with dry cupric oxide in the ratio of 1 to 4 and heated (Figs. 18.11 and 18.12). The carbon present is oxidized to carbon dioxide and the hydrogen to water vapour.

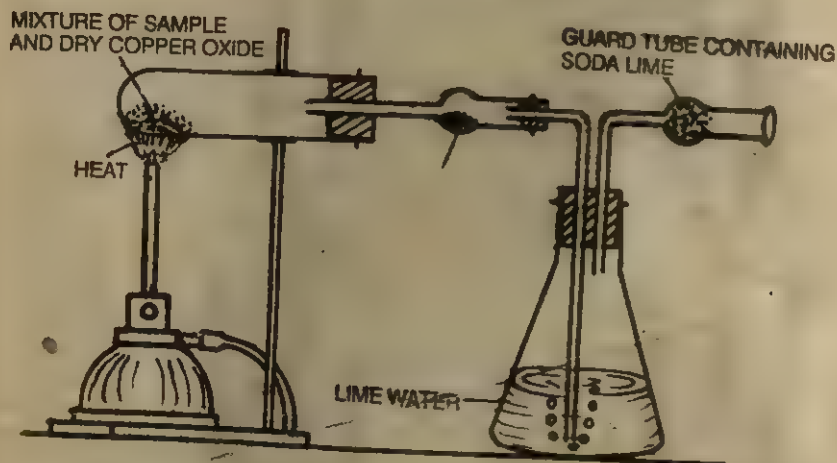
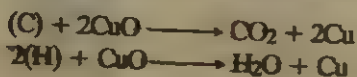
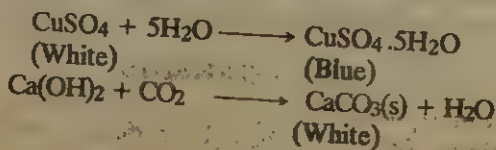


Fig.18.11. Detection of carbon and hydrogen

The gaseous products of reaction are passed first over anhydrous copper sulphate powder (white) and then through lime water. Water vapours turn anhydrous white copper sulphate to hydrated blue copper sulphate. Carbon dioxide turns lime water milky.



18.3.2 Test for Nitrogen

(i) **Heating with soda-lime** : The substance to be tested is mixed with soda-lime and heated. Active component of soda-lime is NaOH. If there is smell of ammonia it indicates the presence of nitrogen. This

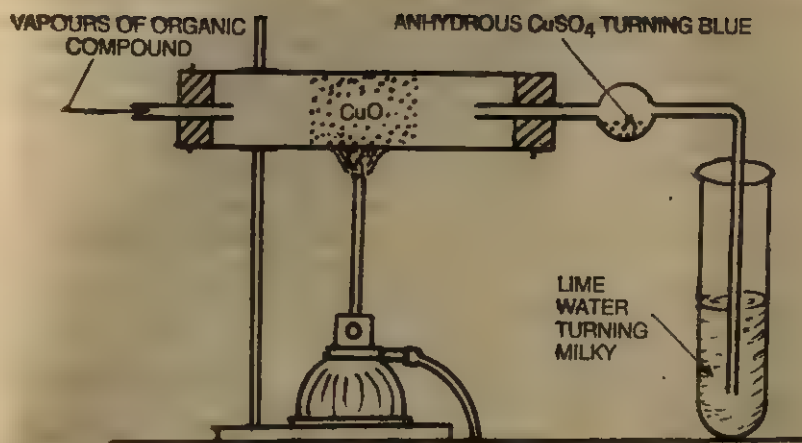


Fig. 18.12 Detection of carbon and hydrogen in a volatile organic liquid or gas

test is positive for amides. Some nitrogen compounds do not respond to this test. (e.g., nitro and diazo compounds).

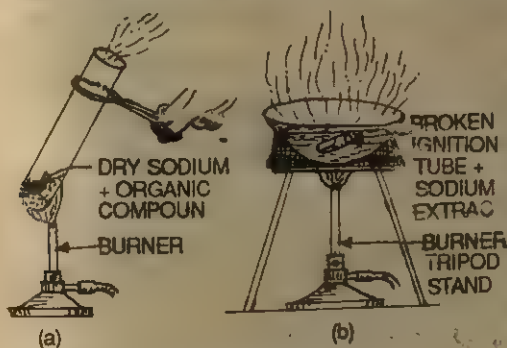
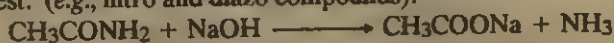
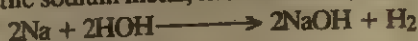


Fig. 18.13. Fusion of organic compound with sodium or potassium

Lassaing's Test : It is the most reliable test for detecting nitrogen as well as sulphur and halogens. The organic compound is fused with sodium or potassium (Fig. 18.13) to convert the element present to the ionic form. This is done by heating a pea-sized piece of sodium metal in a combustion tube. Organic substance is added to the molten

sodium. After some substance has reacted, the heating of the tube is gradually increased to redness. The red hot tube is broken into distilled water kept in a dish. The solution is then heated to boiling for a few minutes. Any of the sodium metal, left unreacted, reacts with water.



The solution is filtered hot (Fig. 18.14). The filtrate contains sodium or potassium salts formed in an alkaline medium (residual excess of the metal gives alkali),

This alkaline solution is called 'Lassaigne's test solution' or sodium extract and is used for the detection of the element.

In this process, the nitrogen of the organic substance is converted to sodium cyanide, sulphur to sodium sulphide or thiocyanate (or sulphocyanide) and the halogens to the respective halides. All these are soluble in water.

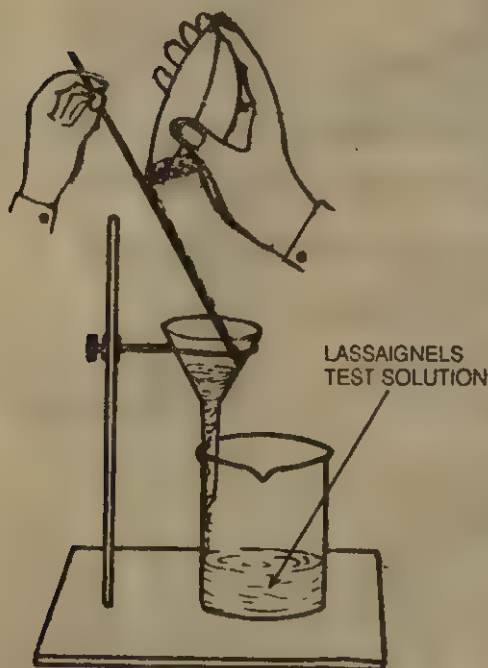
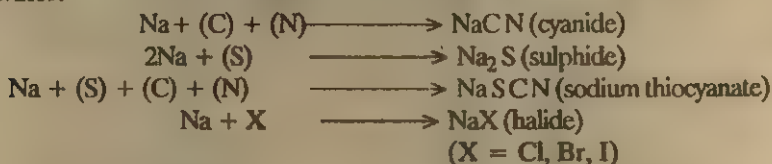


Fig. 18.14. Preparation of Lassaigne's test solution.

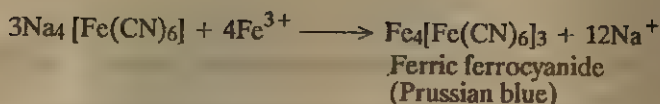
To detect nitrogen, the filtrate is heated with a freshly prepared ferrous sulphate solution when sodium (or potassium) ferrocyanide is formed.



While the solution is being boiled, some ferrous is also oxidized to ferric. When the solution is neutralized with dilute sulphuric acid, ferric reacts with ferrocyanide to give ferric ferrocyanide (Prussian blue).

The solution is filtered hot (Fig. 18.14). The filtrate contains sodium or potassium salts formed in an alkaline medium (residual excess of the metal gives alkali).

This alkaline solution is called 'Lassaigne's test solution' or solution extract and is used for the detection of the element.



This shows the presence of nitrogen in the organic compound.

18.3.3 Detection of Halogens

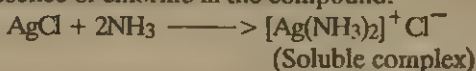
Lassaigne's test solution is boiled with nitric acid to decompose cyanide or sulphide, if present, to volatile hydrogen cyanide and hydrogen sulphide respectively.



The solution is cooled and silver nitrate solution added when silver halide precipitate appears if halogen is present.



A white precipitate (AgCl) soluble in ammonium hydroxide indicates the presence of chlorine in the compound.



Light yellow precipitate (AgBr) sparingly soluble in ammonium hydroxide and yellow precipitate (AgI) insoluble in ammonium hydroxide show the presence of bromine and iodine respectively.

The presence of bromine or iodine in the organic compound may be confirmed by acidifying Lassaigne's test solution with nitric acid and adding a few drop of chlorine water to oxidize the halide present to corresponding halogen. The liberated bromine or iodine is identified by shaking the solution with an organic solvent (chloroform or carbon tetrachloride) when the halogen goes into the solvent layer (Fig.18.15)

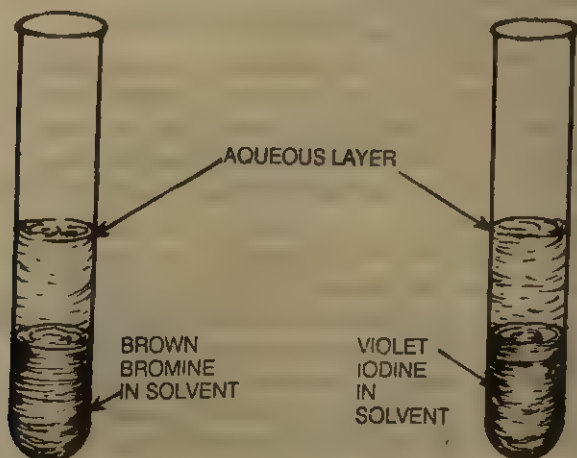
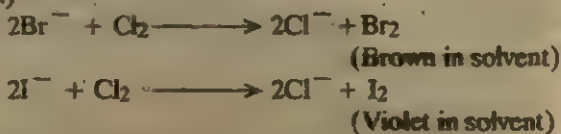


Fig. 18.15. Extraction of bromine or iodine in solvent.

giving it a characteristic colour (brown layer in case of bromine and violet in case of iodine.)



18.3.4 Detection of Sulphur

To one portion of Lassaigne's test solution is added acetic acid and lead acetate. A black precipitate of lead sulphide is formed if sulphur is present in the compound.



To the other portion of the solution is added sodium nitroprusside. The formation of a violet coloured complex shows the presence of sulphur.

18.3.5 Detection of Phosphorus

An organic compound is fused with sodium peroxide. The fused mass is extracted with water. The aqueous extract is boiled with concentrated nitric acid and treated with ammonium molybdate solution. The appearance of a yellow precipitate of ammonium phosphomolybdate, $(\text{NH}_4)_3 [\text{PMo}_{12}\text{O}_{40}]$, indicate the presence of phosphorus in the compound.

18.3.6 Detection of Oxygen

There is no method for the direct detection of oxygen bearing groups such as $-\text{OH}$, $-\text{COOH}$, $-\text{NO}_2$, $-\text{CHO}$, $>\text{C}=\text{O}$, etc.

18.4 QUANTITATIVE ANALYSIS OF ELEMENTS

After the detection of elements present in an organic compound the next step is the quantitative estimation of elements present in it. We shall now describe the methods of estimating hydrogen, nitrogen, halogens, sulphur, phosphorus and oxygen in organic compounds.

18.4.1 Estimation of Carbon and Hydrogen (Liebig's Combustion Method)

In this method carbon and hydrogen are estimated simultaneously. A known mass (W_g) of the organic substance is mixed with an excess of cupric oxide powder and heated in a stream of purified oxygen (CO_2 free). This oxidizes carbon to carbon dioxide and hydrogen to water vapour. The gases are passed over a heated bed of coarse copper oxide to complete the oxidation. The gases produced by combustion are passed through two weighed absorption tubes (or bulbs), the first of which contains anhydrous calcium chloride and the second conc. potassium hydroxide solution (potash bulb). Hydrogen present in the sample of

oxidized to H_2O which is absorbed in an anhydrous CaCl_2 tube (Fig. 18.16). The increase in the mass of this tube (W_1) corresponds to the amount of water produced. The increase in the mass of the bulb (W_2)

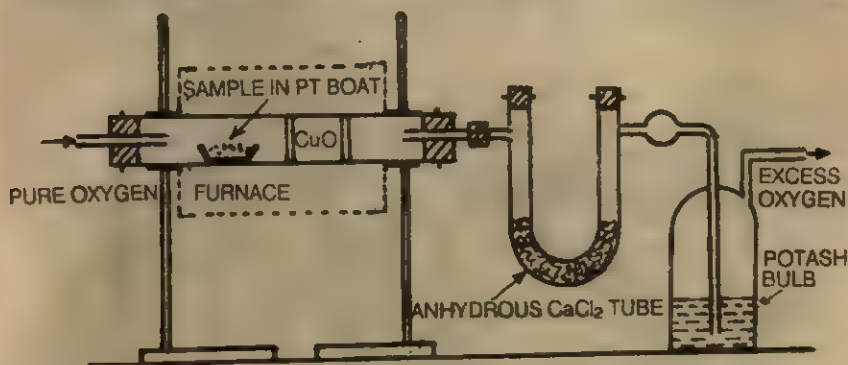


Fig. 18.16. Apparatus for estimation of carbon and hydrogen
corresponds to the mass of CO_2 produced. From these results, the proportion of carbon and hydrogen present in the sample can be calculated.

Now, 44 g of $\text{CO}_2 \equiv 12$ g of carbon

$$\text{Therefore, percentage of carbon} = \frac{12}{44} \times \frac{W_2}{W} \times 100$$

Also, 18g of $\text{H}_2\text{O} \equiv 2$ g of hydrogen

$$\text{Therefore, percentage of hydrogen} = \frac{12}{18} \times \frac{W_1}{W} \times 100$$

Exercise 18.1 In the combustion of 0.2100 g of an organic substance, 0.1620 g of CO_2 and 0.1215 g of water vapour were obtained. Calculate the percentage of carbon and hydrogen in the substance.

$$\text{Solution. Percentage of carbon} = \frac{12 \times 0.162}{44} \times \frac{100}{0.21} = 21.04$$

$$\text{Percentage of hydrogen} = \frac{2 \times 0.1215}{18} \times \frac{100}{0.21} = 6.42$$

18.4.2 Estimation of Nitrogen

Nitrogen can be estimated either by Dumas' method or Kjeldahl's method. Dumas' method is of general application to nitrogen containing organic compounds.

Duma's method

A known mass of an organic compound (W g) is heated with cupric oxide in an atmosphere of carbon dioxide (Fig. 18.17.) Carbon, hydrogen

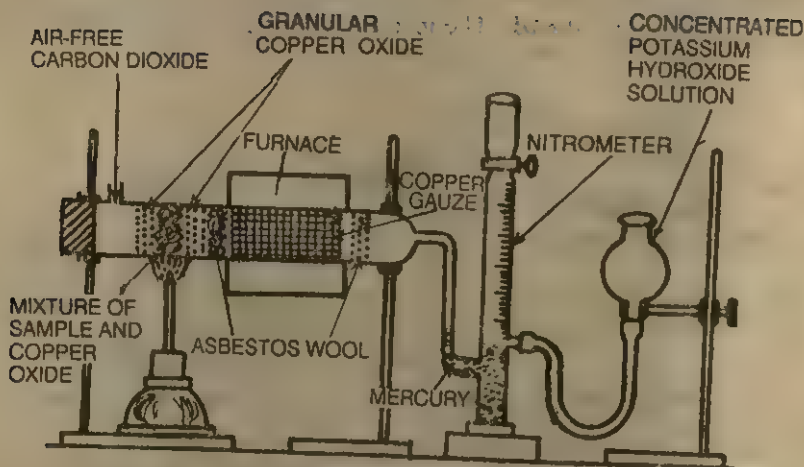


Fig. 18.17. Duma's assembly for estimation of nitrogen.

and sulphur present in the compound are oxidized to CO_2 , H_2O and SO_2 , respectively, while nitrogen is released or possibly converted to some of its oxides. The gaseous mixture is passed over a hot reduced copper gauze to reduce back oxides of nitrogen to free nitrogen. It is then collected in a nitrometer containing concentrated potassium hydroxide solution which absorbs all other gases except nitrogen. The volume of nitrogen collected ($V_1 \text{ mL}$) is noted along with the room temperature ($T_1 \text{ K}$) and atmospheric pressure ($P_1 \text{ mm Hg}$).

Applying gas equation, we obtain :

$$\text{Volume of nitrogen at STP} = \frac{P_1 V_1}{760} \times \frac{273}{T_1} = v \text{ mL}$$

$$\text{Mass of } v \text{ ml of nitrogen at STP} = \frac{28 \times v}{22400} \text{ g}$$

$$\text{Therefore, percentage of nitrogen} = \frac{28 \times v \times 100}{22400 \times W}$$

Exercise 18.2 0.0280 g of an organic compound produced 5.60 cm^3 of nitrogen, measured dry and corrected to STP in Dumas' determination. The density of nitrogen is $0.00125 \text{ g cm}^{-3}$ at STP. 5.60 cm^3 nitrogen weigh $5.60 \times 0.00125 \text{ g}$. Calculate the proportion of nitrogen in the compound.

Solution.

$$\text{Percentage of nitrogen} = \frac{5.60 \times 0.00125 \times 100}{0.0280} = 25.0$$

Kjeldahl's method :

This method can be carried out more easily than Dumas' method. However, it is not applicable to compounds in which nitrogen is directly linked to oxygen.

A known mass of an organic compound (W g) is heated with conc. H_2SO_4 and a small amount of copper sulphate (catalyst) in a long necked pear shaped Kjeldahl's flask (Fig. 18.18a). The method is based on the

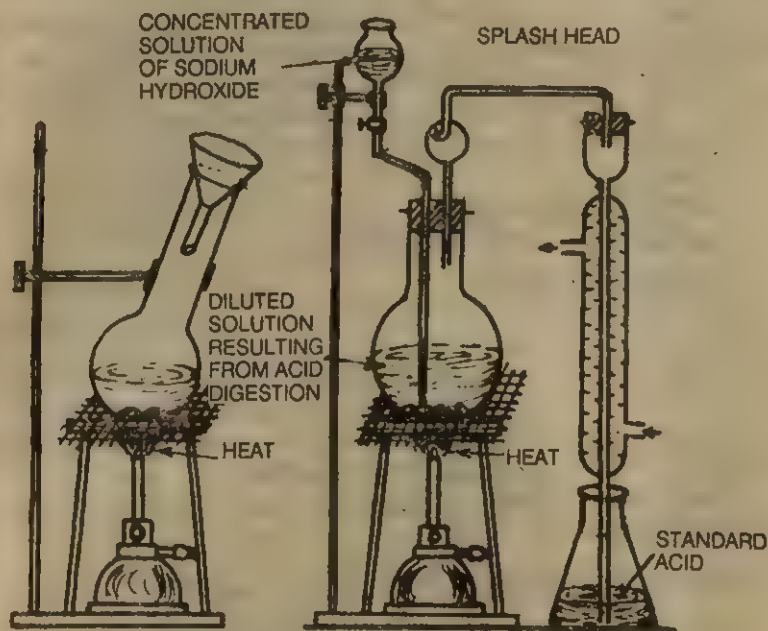


Fig. 18.18. Kjeldahl's assembly for nitrogen determination.

(a) Long-necked Kjeldahl flask in which the organic compound is digested with concentrated sulphuric acid. (b) Ammonia distillation apparatus used in the second stage of the Kjeldahl's determination.

fact that nitrogen in an organic compound can often be converted to ammonia by the prolonged action of hot conc. sulphuric acid, the end product being ammonium sulphate. The contents of the Kjeldahl's flask are transferred to another flask and heated with sodium hydroxide solution (Fig. 18.18 b). The liberated ammonia is distilled over (or absorbed) into a known volume of standard acid (the splash head serves to prevent any sodium hydroxide spray from being carried over into the standard acid). The amount of ammonia liberated is determined by back titrating the excess acid with standard alkali.

The amount of acid neutralized (V_1 mL of normality N_1) is determined by titrating it with a standard alkali and this corresponds to

the amount of ammonia evolved. We know, V_1 ml of normality N_1 acid $\equiv V_1$ mL of normality N_1 ammonia. Now 1000 mL of normal ammonia \equiv 17g of ammonia \equiv 14 g of nitrogen.

$$\text{Thus, } V_1 \text{ ml of } N_1 \text{ ammonia} \equiv \frac{14 V_1 N_1}{1000} \text{ g of nitrogen}$$

$$\text{Hence, percentage of nitrogen} = \frac{14 V_1 N_1}{1000} \times \frac{100}{W}$$

Exercise 18.3 On estimating nitrogen in 1.5250 g of an organic substance by the Kjeldahl method, the ammonia evolved on heating with NaOH solution was absorbed in 30.0 mL of normal H_2SO_4 solution. The residual acid required 120 mL of $N/10$ NaOH for neutralization. Calculate the percentage of nitrogen in the organic substance.

Solution

$$\text{Mass of the substance taken} = 1.5250 \text{ g}$$

$$\text{Volume of normal } \text{H}_2\text{SO}_4 \text{ solution taken} = 30.0 \text{ mL}$$

$$\begin{aligned} \text{Now acid left unused} &= 120 \text{ mL } N/10 \text{NaOH} \\ &\equiv 120 \text{ mL } N/10 \text{H}_2\text{SO}_4 \\ &= 120 \times \frac{1}{10} \text{ or } 12 \text{ mL } N \text{H}_2\text{SO}_4 \end{aligned}$$

Acid neutralized by $\text{NH}_3 = 30 - 12 = 18 \text{ mL } 1 \text{ N } \text{NH}_3 \text{ solution}$
or $18 \text{ mL } 1 \text{ N } \text{H}_2\text{SO}_4 = 18 \text{ mL } 1 \text{ N } \text{NH}_3 \text{ solution}$

But 1,000 mL of normal ammonia solution contains 17g of ammonia or 14 g of nitrogen.

$$1,000 \text{ mL } 1 \text{ N ammonia} \equiv 14 \text{ g nitrogen}$$

$$18 \text{ mL } 1 \text{ N ammonia} \equiv \frac{18}{1000} \times 14 \text{ or } 0.252 \text{ g nitrogen}$$

$$\text{Nitrogen in 1.525 g of substance} = 0.252 \text{ g}$$

$$\text{or percentage of nitrogen} = \frac{0.252}{1.525} \times 100 = 16.5$$

18.4.3 Estimation of Halogens (Carius Method)

A known mass of an organic compound (W g) is heated with fuming nitric acid and a few crystals of AgNO_3 in a sealed hard glass tube known as Carius tube (Fig. 18.19a). The sealed tube is placed in an iron socket tube heated in a special furnace. The furnace temperature is maintained near 475K (Fig. 18.19b) for six to seven hours and then the furnace is allowed to cool down to room temperature. The halogen part of the substance is converted to the corresponding silver halide. After breaking

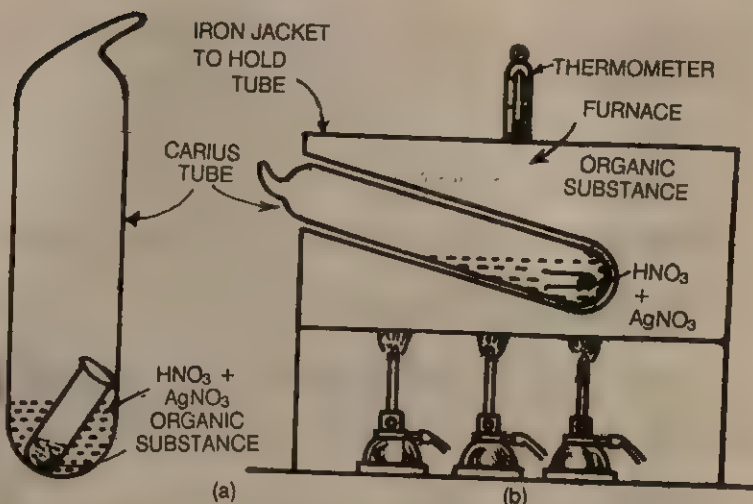


Fig. 18.19. Estimation of halogen by Carius method.

the seal, the contents of the Carius tube are collected. Silver halide is filtered, washed, dried and weighed. Percentage of the halogen is then calculated from the mass of silver halide formed.

Let the amount of AgX produced be $W_1\text{g}$. We know,
Atomic mass of X = Molecular mass of AgX

Thus,

Mass of halogen in $W_1\text{ g}$ of AgX

$$= \frac{\text{Atomic mass of X} \times W_1\text{g}}{\text{Molecular mass of AgX} \times W_1\text{g}}$$

Therefore, percentage of halogen

$$= \frac{\text{Atomic mass of X} \times W_1\text{g}}{\text{Molecular weight of AgX} \times W_1\text{g}} \times 100$$

Exercise 18.4 In a Carius estimation 0.1890 g of a chloro-compound gave 0.2870 g of AgCl precipitate. Calculate the percentage of chlorine in the compound.

Solution: Chlorine in 143.5 g of AgCl = 35.5 g

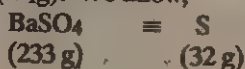
$$\text{Chlorine in 0.2870 g of AgCl} = \frac{0.287}{143.5} \times 35.5 = 0.071\text{ g}$$

$$\text{Percentage of chlorine} = \frac{0.071}{0.189} \times 100 = 37.6$$

18.4.4 Estimation of Sulphur

A known mass of an organic compound ($W\text{g}$) is heated with fuming nitric acid and barium chloride acid in a Carius tube (Fig. 18.19). The sulphur present is oxidized to sulphuric acid. The acid, thus, produced is

precipitated as barium sulphate. The precipitate is filtered, washed, dried and weighed (W_1 g). We know,



233 g of BaSO_4 contain 32 g of sulphur

Therefore, W_1 g of BaSO_4 will contain $\frac{32}{233} \times W_1$ g of sulphur

Hence percentage of sulphur $= \frac{32}{233} \times \frac{W_1}{W} \times 100$

Exercise 18.5 In a Carius estimation 0.2595 g of an organic compound gave 0.3500 g of BaSO_4 precipitate. What is the percentage of sulphur in the compound ($\text{Ba} = 137.34$, $\text{S} = 32.0$, $\text{O} = 16.0$).

Solution

Molecular mass of $\text{BaSO}_4 = 137.34 + 32.0 + 16.0 = 233.34$

Sulphur in 233.34 g of $\text{BaSO}_4 = 32.0$ g

Sulphur in 0.3500 g of $\text{BaSO}_4 = \frac{0.35 \times 32.0}{233.34} = 0.0479$ g

Percentage of sulphur $= \frac{0.0479}{0.2596} \times 100 = 18.5$

18.4.5 Estimation of Phosphorus

A known mass of an organic compound (W g) is heated with fuming nitric acid in a Carius tube (Fig. 18.19) and the phosphorus present is oxidized to phosphoric acid (H_3PO_4). The acid, thus, produced is treated with magnesia mixture (magnesium chloride, ammonium chloride and ammonium hydroxide). A precipitate of magnesium ammonium phosphate ($\text{Mg NH}_4\text{PO}_4$) is obtained which on ignition yields W_1 g of magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$).

We know,

$$\begin{array}{ccc} \text{Mg}_2\text{P}_2\text{O}_7 & \equiv & 2\text{P} \\ (222 \text{ g}) & & (62 \text{ g}) \end{array}$$

22 g of $\text{Mg}_2\text{P}_2\text{O}_7$ contains 62 g of phosphorus

Therefore, W_1 g of $\text{Mg}_2\text{P}_2\text{O}_7$ will contain $\frac{62}{222} \times W_1$ g of phosphorus

Hence, percentage of phosphorus $= \frac{62}{222} \times \frac{W_1}{W} \times 100$

18.4.6 Estimation of Oxygen

The percentage of oxygen in an organic compound is determined by subtracting the sum of the percentages of all other elements from 100.

Exercise 18.6 From 0.2100 g of an organic substance 0.4620 g of CO_2 and 0.1215 g of H_2O were formed. On heating 0.1040 g of the same substance with caustic soda yielded all its nitrogen as ammonia, neutralization of which needed 15 mL of $N/20 \text{ H}_2\text{SO}_4$. If oxygen is a only other element present in the substance, what is its percentage in the substance?

Solution :

$$\text{Percentage of carbon in the substance} = 0.462 \times \frac{12}{44} \times \frac{100}{0.21} = 60.0$$

$$\text{Percentage of hydrogen in the substance} = 0.1215 \times \frac{2}{18} \times \frac{100}{0.21} = 6.43$$

$$\text{Now, 17 g of } \text{NH}_3 \quad \quad \quad \equiv 14 \text{ g of nitrogen}$$

$$\text{Ammonia evolved on heating with NaOH} \equiv 15 \text{ mL of } \frac{N}{20} \text{ H}_2\text{SO}_4$$

$$= 15 \text{ mL of } \frac{N}{20} \text{ NH}_3 \text{ Solution.}$$

$$\text{But 1000 mL of } 1N \text{ NH}_3 \text{ solution.} \quad \equiv 14 \text{ g of Nitrogen}$$

$$15 \text{ ml of } \frac{N}{20} \text{ NH}_3 \text{ solution.} \equiv \frac{14}{1000} \times \frac{15}{20} \text{ g of Nitrogen}$$

$$\text{Percentage of nitrogen in the substance} = \frac{15 \times 14}{1000 \times 20} \times \frac{100}{0.104} = 10.09$$

$$\text{Sum of percentage of C, H and N} = 60.00 + 6.43 + 10.09 = 76.52$$

$$\begin{aligned} \text{Percentage of oxygen} &= 100 - 76.52 \\ &= 23.48 \end{aligned}$$

18.5 DETERMINATION OF MOLECULAR MASS

Molecular mass (*i.e.*, the mass of one molecule as compared to the mass of one atom of oxygen taken as 16 or carbon taken as 12) of a substance may be determined either by physical methods (Victor Meyer, freezing point depression or boiling point elevation) or chemical methods (volumetric).

18.5.1 Victor Meyer's Method

A known mass of an organic compound (W g) is converted to its vapour (in Victor Meyer's apparatus, Fig. 18.20) The vapour is made to displace an equal volume of air (V_1 mL) which is collected in a graduated tube over water. The pressure of air (P mm Hg) and the room temperature (T_1 K) are also noted. Applying the gas equation, we obtain:

$$\text{Volume } V_2 \text{ of air displaced at STP} = \frac{P \times V_1 \times 273}{T_1 \times 760}$$

Now V_2 mL of vapour of the substance at STP weighs W g. Therefore, 22 400 mL of vapour of the substance at STP will weigh $W \times \frac{22\,400}{V}$

which is equal to the molecular mass of the substance.

18.5.2 Molecular Mass by Elevation of Boiling Point or Depression of Freezing Point

The molecular mass of a non-volatile organic compound can be determined by measuring elevation in boiling point of a solvent by dissolving a known mass of the compound (solute) in a known quantity of the solvent. Similarly with the addition of a substance the freezing point of the solvent is lowered down.

(i) **Elevation of boiling point:** The boiling point of a liquid is the temperature at which the vapour pressure of the liquid is equal to the

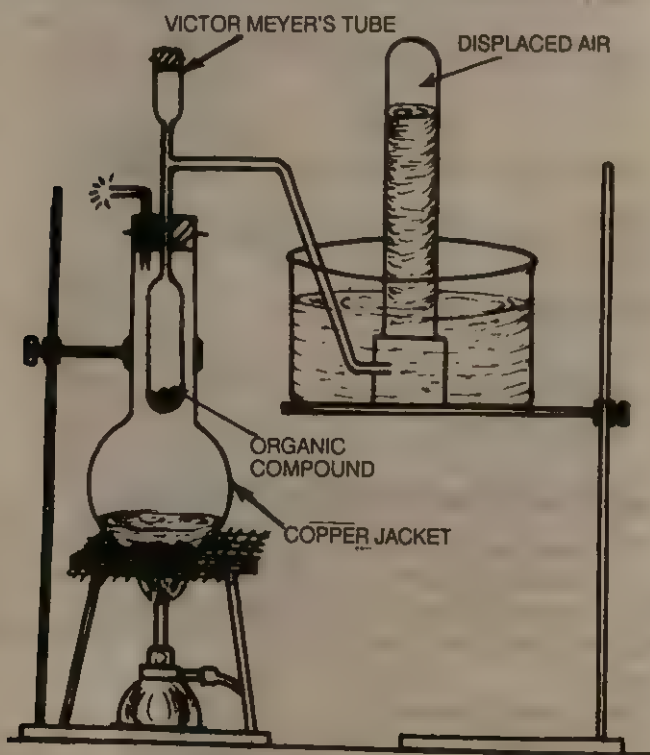


Fig. 18.20. Victor Meyer's apparatus

atmospheric pressure. The vapour pressure of a solvent reduces on addition of a non-volatile solute. Thus, to make vapour pressure equal to atmospheric pressure, we will have to heat the solution to a higher

temperature. This means that the boiling point of the solution is higher than the pure solvent.

(ii) **Depression of freezing point:** The freezing point of a liquid is the temperature at which the vapour pressure of the liquid and the solid states of the substance are the same. It has been found that the freezing point of a solution lowers down on addition of a non-volatile solute in the solvent. The apparatus used for the determination of molecular mass by depression in freezing point is shown in Fig. 18.21.

Using the equation,

$$\Delta T_f = \left[\frac{K M_A}{1000} \right] m = K_f m$$

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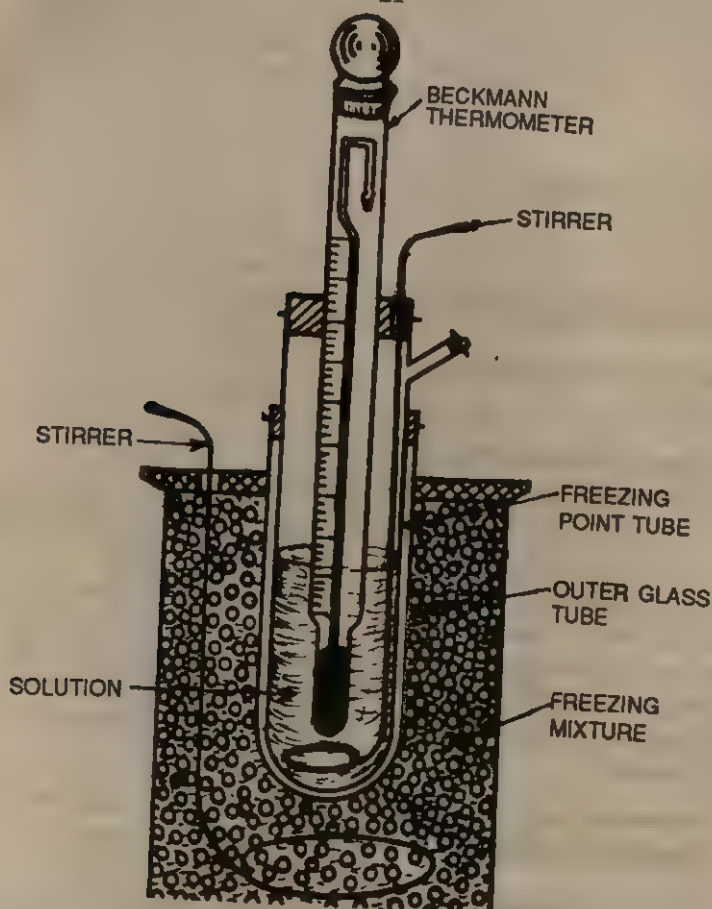


Fig. 18.21. An assembly for the determination of depression of freezing point.

Where ΔT_f = depression in freezing point

K_f = constant M_A = Molecular mass of compound.

m = molality

Exercise 18.7 In a Victor Meyer's experiment 0.100 g of a liquid on evaporation gave 25.0 mL of displaced air. The water temperature in the gas measuring tube was 293K and the barometer reading was 750 torr. Aqueous tension at 293K equals 17.4 torr. Calculate the molecular mass of the liquid.

Solution :

Here mass of liquid, $w = 0.1$ g; $P_1 = 750 - 17.4 = 732.6$ torr, $V_1 = 25.0$ mL; $T_1 = 293$ K; T_2 (at STP) = 273 K; $P_2 = 760$ torr; $V_2 = ?$

We know $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\frac{732.6 \times 25}{293} = \frac{760 \times V_2}{273}$$

$$\text{Volume at STP, } V_2 = \frac{273 \times 732.6 \times 25}{293 \times 760}$$

$$= 22.46 \text{ mL or } 0.02246 \text{ L}$$

Mass of 0.02246 L at STP of vapour = 0.100 g

$$\text{or mass of } 22.4 \text{ L at STP of vapour} = \frac{22.4}{0.02246} \times 0.100 = 99.95 \text{ g}$$

Hence, the molecular mass of liquid = 99.95

18.5.3 Volumetric Methods (for Acids and Bases)

In this method a known quantity of the substance is dissolved in distilled water or purified alcohol and the solution is made up to a known volume. A measured volume of this acid (or base) solution is then titrated against a standard solution of strong alkali (or acid) using an appropriate indicator (phenolphthalein or methyl orange). From the titre value, chemical equivalent of the solute can be calculated. Knowing the acidity (in case of a base) or basicity (in case of an acid) molecular mass can be obtained.

For acids : Let V_1 mL of N_1 alkali be used for neutralization. Then, V_1 mL of N_1 alkali \equiv Wg of acid

$$1000 \text{ mL of normal alkali} = \frac{W}{V_1} \times \frac{1000}{N_1} \text{ g of acid}$$

Now, 1000 mL of normal alkali contain 1 g equivalent of the alkali and it should neutralize 1 g equivalent of the acid.

$$\text{Therefore, equivalent mass of the acid} = \frac{W}{V_1} \times \frac{1000}{N_1}$$

$$\text{Molecular mass of the acid} = \left(\frac{W}{V_1} \times \frac{1000}{N_2} \right) \times \text{Basicity of acid.}$$

For bases : A known mass of a base (W g) is dissolved in water or alcohol and titrated with a standard acid. If V_1 ml of N_1 acid is used for neutralization, then proceeding as before, we obtain .

$$\text{Molecular weight of the base} = \left(\frac{W}{V_1} \times \frac{1000}{N_1} \right) \times \text{Acidity of base.}$$

Exercise 18.8 : On combustion 0.200 g of a monobasic organic acid gave 0.505 g CO_2 and 0.0892 g water. For neutralization 0.183 g of the acid dissolved in water 15mL of $N/10$ NaOH were required. Calculate the molecular mass and the molecular formula of the acid.

Solution :

$$\text{Percentage of carbon in the acid} = \frac{12}{44} \times 0.505 \times \frac{100}{0.2} = 68.86$$

$$\text{Percentage of hydrogen in the acid} = \frac{2}{18} \times 0.0892 \times \frac{100}{0.2} = 4.95$$

$$\begin{aligned} \text{Percentage of oxygen} &= 100 - (68.86 + 4.95) = 26.19 \\ \text{(by difference)} \end{aligned}$$

18.6 CALCULATION OF EMPIRICAL AND MOLECULAR FORMULAE

The empirical formula of a compound represents the simplest whole number ratio of the atoms of various elements present in the molecule. In order to determine the empirical formula:

(i) Divide the percentage composition of different elements by their respective atomic masses. This gives the atomic ratio (i.e. relative number or atoms).

(ii) Divide each of the atomic ratios by the lowest one amongst them to obtain the simple ratios of the various elements in the compound.

(iii) If the figures of the simple ratios are not whole numbers they are converted to whole numbers by multiplying with a suitable common factor.

Exercise 18.9 : An organic compound contains 54.5% C and 9.09% H. Calculate its empirical formula.

$$\text{Solution : Percentage of oxygen} = 100 - (54.5 + 9.09) = 36.41$$

Element	Percentage	Atomic mass	Relative number of atoms	Simple ratio (Dividing by the smallest factor)	Simple whole number ratio
Carbon	54.50	12	$\frac{54.50}{12} = 4.50$	$\frac{4.54}{2.27} = 2$	2
Hydrogen	9.09	1	$\frac{9.09}{1} = 9.09$	$\frac{9.09}{2.27} = 4$	4
Oxygen	36.41	16	$\frac{36.41}{16} = 2.27$	$\frac{2.27}{2.27} = 1$	1

Empirical formula is C_2H_4O

Exercise 18.10 : 0.1890 g of an organic compound gave 0.1760 g of CO_2 and 3.0544 g of H_2O . 0.2079 g of the substance produced 0.3157 g of $AgCl$ by Carius method. Determine the empirical formula of the substance.

Solution :

$$\begin{aligned} \text{Percentage of carbon} &= \frac{12 \times \text{mass of } CO_2 \times 100}{44 \times \text{mass of compound}} \\ &= \frac{12 \times 0.1760 \times 100}{44 \times 0.1890} = 25.40 \end{aligned}$$

$$\begin{aligned} \text{Percentage of hydrogen} &= \frac{2 \times \text{mass of water} \times 100}{18 \times \text{mass of compound}} \\ &= \frac{2 \times 0.0540 \times 100}{18 \times 0.8890} = 3.17 \end{aligned}$$

$$\begin{aligned} \text{Percentage of chlorine} &= \frac{35.5 \times \text{mass of } AgCl \times 100}{143.5 \times \text{mass of compound}} \\ &= \frac{35.5 \times 0.3157 \times 100}{143.5 \times 0.2079} = 37.57 \end{aligned}$$

$$\text{Percentage of oxygen} = 100 - (25.40 + 3.17 + 37.57) = 33.86$$

Element	Atomic mass	Percentage	Relative number of atoms	Simple ratio (Dividing by the smallest factor)	Simple whole number ratio
C	12	25.40	$\frac{25.40}{12} = 2.12$	$\frac{2.12}{1.06} = 2$	2
H	1	3.17	$\frac{3.17}{1} = 3.17$	$\frac{3.17}{1.06} = 3$	3
Cl	35.5	37.57	$\frac{37.75}{35.5} = 1.06$	$\frac{1.06}{1.06} = 1$	1
O	16	33.86	$\frac{33.86}{16} = 2.12$	$\frac{2.12}{1} = 2$	2

Hence, the empirical formula is $C_2H_3ClO_2$

The molecular formula represents the actual number of atoms of different elements present in a molecule of a compound. In order to determine the molecular formula of a compound, we require :

(i) empirical formula and empirical formula mass

(ii) Molecular mass

Molecular formula and empirical formula can either be the same or the former is a simple multiple of the latter. Thus, Molecular formula = $n \times$ Empirical formula

(where $n = 1, 2, 3$ etc. and is obtained by dividing the molecular mass by empirical formula mass).

If n is not a whole number, it is changed to the nearest whole number.

Exercise 18.11 : On combustion, 0.152 g of an organic compound gave 0.304 g of CO_2 and 0.124 g of H_2O . The vapour density of the compound was 44. Calculate its molecular formula.

Solution :

$$\text{Percentage of carbon} = \frac{12 \times 0.304 \times 100}{44 \times 0.152} = 54.55$$

$$\text{Percentage of hydrogen} = \frac{2 \times 0.124 \times 100}{18 \times 0.152} = 9.06$$

$$\text{Percentage of oxygen} = 100 - (54.55 + 9.06) = 36.39$$

Element	Atomic mass	Per-centage	Relative number of atoms	Simple ratio	Simple whole number ratio
C	12	54.55	$\frac{54.55}{12} = 4.55$	$\frac{4.55}{2.27} = 2$	2
H	1	9.06	$\frac{9.06}{1} = 9.06$	$\frac{9.06}{2.27} = 4$	4
O	16	36.39	$\frac{36.39}{16} = 2.27$	$\frac{2.27}{2.27} = 1$	1

Hence, the empirical formula is $\text{C}_2\text{H}_4\text{O}$

$$\text{Empirical formula mass} = (2 \times 12 + 4 \times 1 + 1 \times 16) = 44$$

$$\text{Molecular weight of the compound} = \text{vapour density} \times 2 = 44 \times 2 = 88.$$

$$\text{Therefore, } n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{88}{44} = 2$$

$$\begin{aligned} \text{Hence, the molecular formula} &= n \times \text{Empirical formula} \\ &= 2 \times (\text{C}_2\text{H}_4\text{O}) = \text{C}_4\text{H}_8\text{O}_2 \end{aligned}$$

18.7 MODERN METHODS OF STRUCTURE ELUCIDATION

It has been possible to establish the structure of a compound by the help of new scientific instruments and devices: X-ray diffraction, NMR, mass spectrometer *etc.* Molecular masses and molecular formulae can be easily determined by mass spectrometry. The nature of functional group present in the organic compound is established from electronic, infrared and nuclear magnetic resonance spectroscopic methods. X-ray diffraction studies help us to determine the bond length, bond angles and the three dimensional structure of the molecule. The detailed studies of these modern tools will be taken up in higher classes.

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions :

18.1 Put tick (✓) mark against the suitable choice:

- A mixture of water and ethyl alcohol is known as (homogeneous, heterogeneous)
- A mixture of chloroform and benzene can be separated by (distillation, sublimation or filtration).
- On sublimation of a mixture of sand, sulphur, iodine and common salt, the sublimate will be (sand, sulphur, iodine, common salt).
- A mixture of sugar, sand and sodium chloride is dissolved in water and then filtered through a filter paper. The residue will be (sugar, sand, sodium chloride).
- Conversion of a solid directly to vapours is called (distillation, sublimation, evaporation).
- The Tyndall effect is shown by a liquid, it must be a (true solution, colloidal solution, pure liquid).
- The melting point of a substance varies over a range of temperature. The substance is (pure, impure).

18.2 Fill in the blanks

- Milk is a _____ solution.
- A mixture of benzene and water can be separated by a process called _____.
- The mixture does not have a _____ composition.
- A compound cannot be separated into its constituent elements by _____ means.
- Smoke is a mixture of _____ and _____.
- The purity of a substance can be tested by determining its _____.
- Distillation is a method for purifying _____.

18.3 Choose the true statements of the following :

- Solutions are homogeneous mixtures of only two substances.
- On heating, a pure substance melts over a range of temperature.
- Two miscible liquids are separated using a separating funnel.
- A mixture of iron filings and sulphur can be separated using carbon disulphide.
- In a solution, the dissolved substance is called the solute and the substance is called the solvent.
- When two liquids, A (b.p. 110°C) and B (b.p. 80°C) are distilled, liquid B would be distilled first.
- A mixture of wood and sand can be separated by filtration method.

TERMINAL QUESTIONS

- How can an organic substance be separated from a mixture of organic and inorganic substances ?
- Describe some methods for the separation of similar substances from mixtures.
- How are the components of a liquid mixture separated ?
- Explain the process of "fractional distillation" and "steam distillation".
- Describe the general method of purifications of liquids.
- How can we show the presence of carbon, hydrogen, and oxygen in an organic substance ?

- 18.7. Describe the detection of nitrogen, sulphur and iodine in an organic substance giving equations wherever possible.
- 18.8 Describe the test for identifying halogens in organic compounds.
- 18.9 Outline the steps involved in the characterization of organic compound.
- 18.10 How can an organic compound be purified? Give examples of (i) crystallization, (ii) sublimation and (iii) distillation.
- 18.11 Give a brief account of various types of distillation processes with which you are familiar.
- 18.12 Describe Liebig's method of estimating carbon and hydrogen in an organic compound.
- 18.13 0.36 g of an organic compound gave 0.01 mole of CO_2 and 0.005 mole of H_2O . Calculate the percentage of carbon and hydrogen in the compound.
(Ans. C 33.3%, H 2.77%).
- 18.14 Explain the principle involved in estimating nitrogen by (i) Duma's method and (ii) Kjeldahl's method.
0.1124 g of an organic compound gave 19.0 mL of nitrogen at 189K and 753.5 mm pressure. Aqueous tension at 289K = 13.5 mm. Calculate the percentage of nitrogen
(Ans. 18.91%)
- 18.15 How is a halogen estimated by Carius method?
0.284 g of an organic compound gave 0.287 g of AgCl on heating with fuming nitric acid and silver nitrate in a Carius tube. Find out the percentage of chlorine in the compound.
(Ans. 25%)
- 18.16 How is sulphur present in an organic compound estimated?
0.32 g of an organic substance containing sulphur gave 0.2334 g of BaSO_4 . Calculate the percentage of sulphur in the substance. Atomic masses of Ba, S and O are 137, 32 and 16 respectively.
(Ans. 10.2%)
- 18.17 Describe the methods of (i) detecting, and (ii) determining phosphorus in a given organic compound.
1.475 g of an organic compound gave 0.7085 g of $\text{Mg}_2\text{P}_2\text{O}_7$. What is the percentage of phosphorus in the compound.
(Ans. 13.42%)
- 18.18 What are the methods of determining the molecular mass of a substance? Describe one of these methods.
- 18.19 An organic compound contained C = 20.0% and H = 6.66%. 0.075 g of this compound, after digestion with conc. H_2SO_4 was distilled with caustic soda and the ammonia evolved was absorbed in 100 mL of 1N H_2SO_4 . The excess of the acid required 73.7 mL 1 N NaOH for neutralization. The molecular mass of the compound was determined to be 60. Find out the molecular formula of the compound.
(Ans. $\text{CH}_4\text{N}_2\text{O}$)
- 18.20 An organic acid was found to contain C = 40% and H = 6.66%. The molecular mass of the acid is 90. Calculate its molecular formula.
(Ans. $\text{C}_3\text{H}_6\text{O}_3$)
- 18.21 0.295 g of an organic compound gave 0.444 g of CO_2 , 0.225 g of H_2O and 56.0 mL of nitrogen at STP. What is the empirical formula of the compound?
(Ans. $\text{C}_2\text{H}_5\text{NO}$)
- 18.22 An organic compound contained C = 53.33%, H = 15.56% and rest of it was nitrogen. Calculate the molecular formula of the compound assuming it to contain one atom of nitrogen per molecule
(Ans. $\text{C}_8\text{H}_7\text{N}$)

ANSWERS TO SELF ASSESSMENT QUESTIONS

- | | | | | |
|------|-----------------|-------------------------------|-----------------------|---------------|
| 18.1 | (i) homogeneous | (ii) distillation | (iii) iodine | (iv) sand |
| | (v) sublimation | (vi) colloidal solution | (vii) impure. | |
| 18.2 | (i) colloidal | (ii) separating funnel method | (iii) definite | (iv) physical |
| | (v) carbon, air | (vi) melting point | (vii) impure liquids. | |
| 18.3 | (i) T | (ii) F | (iii) F | (iv) T |
| | (v) T | (vi) T | (vii) F | |

UNIT 19

The Molecules of Life

"You shall gain your bread by the sweat of your brow until you return to the ground; for from it you were taken. Dust you are, to dust you shall return".
Genesis 3 : 19

UNIT PREVIEW

- 19.1 Introduction
- 19.2 The cell
- 19.3 Carbohydrates
 - 19.3.1 Classification
 - 19.3.2 Monosaccharides
 - 19.3.3 Oligosaccharides
 - 19.3.4 Polysaccharides
 - 19.3.5 Preparation of glucose
- 19.4 Proteins
 - 19.4.1 Amino acids
 - 19.4.2 Peptide bond
 - 19.4.3 Structure of proteins
 - 19.4.4 Chemical characteristics of proteins
 - 19.4.5 Enzymes
- 19.5 Nucleic acids
 - 19.5.1 Structure of nucleic acids
 - 19.5.2 Biological functions of nucleic acids
 - 19.5.3 Viruses
- 19.6 Lipids
- 19.7 Cell defence (medicines, vaccines)
 - Self assessment questions
 - Terminal questions
 - Answers to self assessment questions

LEARNING OBJECTIVES

At the completion of this unit, you shall be able to:

1. Give a definition of biochemistry and macromolecules
2. Describe a living cell and its functions
3. Describe the natural sources of carbohydrates and their chemical compositions.
4. Classify the carbohydrates and describe each of them
5. Define proteins and their major functions
6. Describe the bonding and structure of peptide chain in the α -helix and beta pleated sheet.
7. Understand the meaning of the following terms associated with proteins : Fibrous, globular, α - amino acid, asymmetric carbon atom, chiral centre, peptide bond, denaturation, primary, secondary and tertiary condensation.
8. Explain the importance of enzymes
9. Describe the structures of nucleosides, nucleotides, and the DNA double helix.
10. Know the basic composition of nucleic acids
11. Describe the important biological functions of nucleic acids
12. Understand the term virus, and explain how does virus cause disease.
13. Describe the chemical constituent of cell membrane and their importance
14. Define the following terms: saponification, hydrogenation, replication, transcription, gene, triple, codon, anticodon, photosynthesis, fatty acids, specificity and selectivity.
15. Emphasize and understand the importance of the macromolecules for our living system.

19.1 INTRODUCTION

The lines given in the beginning of this unit suggests man's relationship to NATURE and its laws. But there exists a fascinating interlude between dust to dust – that which we call LIFE. A living organism organizes beautifully to maintain a low entropy within itself, and thus, resists, for a time, the universal tendency to approach a state of equilibrium where entropy and disorder reach a maximum. To maintain and sustain the high degree of order, the living state requires the information of heredity, the energy of biochemical reactivity and sufficient raw materials to build cells.

In man's attempt to understand the physical universe, the complexity of living systems has always presented a challenge.

All life processes - such basic functions as reproduction, growth, movement, thinking and ageing - depend on chemical reactions. Biochemistry is the science that concerns the chemistry of living organisms. It deals with all the substances that make up living matter and with the chemical changes that give rise to life.

Many of the molecules found in living cells are structurally and functionally among the most complex organic substances known to mankind. Living organisms mainly consist of water, proteins, carbohydrates, lipids (fats and oils) nucleic acids and inorganic substances. Oxygen, carbon, hydrogen, and nitrogen are the most abundant elements in living organisms. They account for 96% of body mass. Others, *i.e.*, calcium, phosphorus, potassium, sulphur, chlorine, sodium and magnesium are elements which are found in less abundance in living organisms. Vitamins, enzymes, and hormones are some of the basic functioning components of living cells. In this unit we shall study the chemistry of carbohydrates, proteins and nucleic acids and their specific roles in the maintenance of life.

19.2 THE CELL

The cell is the fundamental unit of all life. Cells combine to form tissues; tissues make into organs; and organs combine into organisms. Cells are too small to be seen by naked eye. They were first seen over 300 years ago with microscope (constructed around that time only). Two views of a typical cell are suggested through Figs. 19.1 and 19.2. Figure 19.1 describes the types and complexity of organic molecules present in cells and Fig 19.2 gives the simplified sub-structure of a cell.

There are various forms of life -- from one celled plants and animals to the highest forms of complexity. Still there is much that these forms of life share. Of the known elements, about 50 occur in living matter in measurable amounts. Of these, about 22 have functions that are known with certainty. Table 19.1 gives the picture of some of the elements that are present in the human body.

TABLE 19.1 Elements present in the human body

Element	Percent by mass	Element	Percent by mass
Carbon	18	Oxygen	65
Calcium	2	Phosphorus	1.2
Chlorine	0.20	Potassium	0.20
Hydrogen	10	Sodium	0.11
Magnesium	0.04	Sulphur	0.20
Nitrogen	3		
Trace Elements : B, Al, Si, V, Mn, Fe, Co, Cu, Zn, Mo, I.			

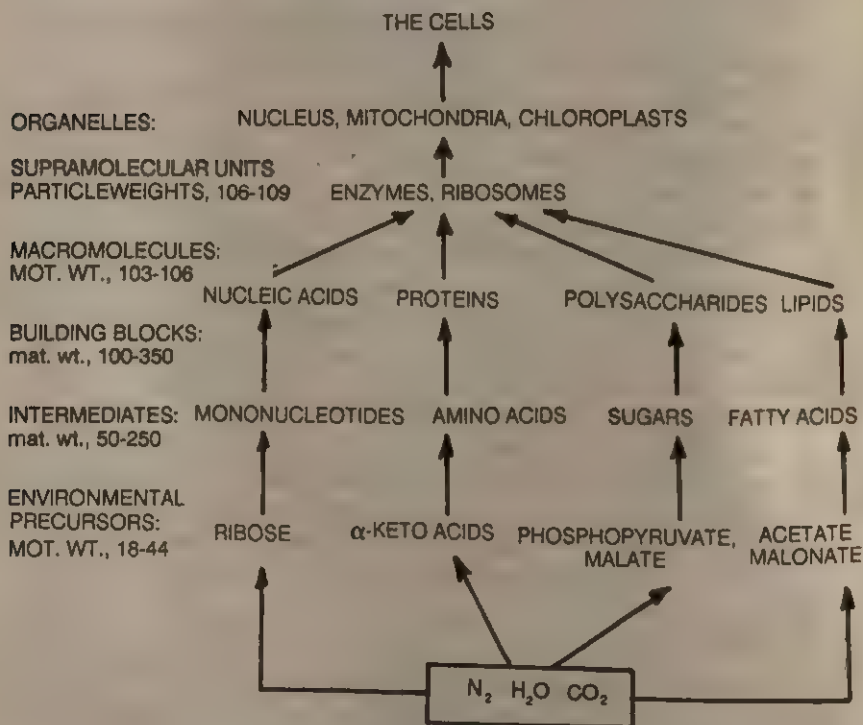


Fig. 19.1 Cellular organisation

Water is the principal constituent of living matter (Table 19.2). Most plants and animals contain 65-90 percent of water by mass. The percentage of water varies with the kind of organism and with the organ or tissue concerned, e.g., bones contain 12 to 15 percent of water whereas the water content of the blood is about 80 percent. Water keeps the inorganic substances and organic molecules in solution, by which they are transported through the living organisms. Foods, when digested, are taken to various parts of the body in fluid form. Many waste products are eliminated from the body as water soluble substances. The oxygen which we breathe dissolves in water before it is carried to blood by the tis-

sues of lungs. Plants take their food from the soil in aqueous solution. Food produced in the leaves of plants passes in solution form to the roots

TABLE 19.2 Approximate chemical composition of bacterial cell

Substance	Percent by mass	Substance	Percent by mass
Water	70	Nucleic acids	
		DNA	1
		RNA	6
Elements (Na^+ , K^+ , Mg^+ , Ca^{2+} , etc.)	1	Phospholipids	2
Polysaccharides	2	Other small molecules	3
Proteins	15		

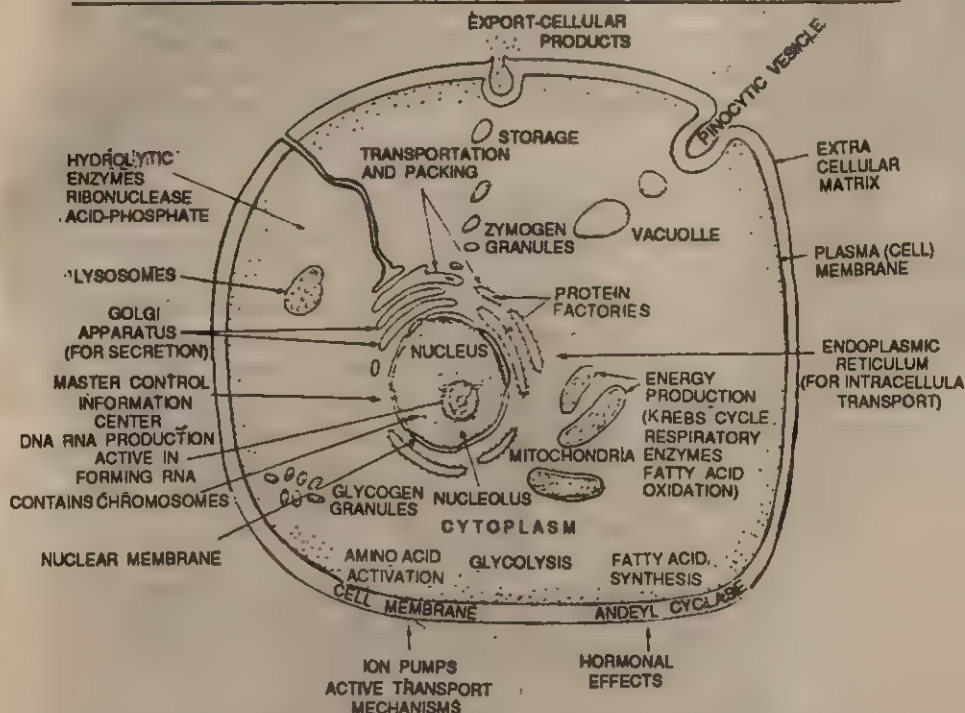


Fig. 19.2 A typical animal cell and its sub structural components

1. The outer wall of the cell, plasma membrane separates the extra-cellular matrix and the cytoplasm of the cell.
2. Golgi apparatus is a membrane covered flat sac which contains macromolecules for secretion and delivery to other organelles.
3. The endoplasmic reticulum present in eukaryotic cells contains on its outer surface ribosomes which synthesize protein.
4. The nucleus is equipped with chromosomal DNA packed with histone proteins.
5. Mitochondria are the power plants of all eukaryotic cells which derive energy from food to produce ATP.
6. Lysosomes contain hydrolytic enzymes which are involved in intracellular digestion.

and seeds. Next to water, carbon is found in the form of micro as well as macromolecules. Micromolecules whose mass is in the range of 100 to 1000 amu contain ~ 30 carbon atoms and are found free in solution in the cytoplasm of the cell. These molecules get converted to macromolecules through various stages.

The chemical reactions which take place in the course of synthesizing the organic molecules - micro and macro - are given a collective name 'metabolism'. Two types of metabolisms are catabolism and anabolism. **Catabolism** relates to the breakdown of organic molecules, e.g., breaking of sugar into carbon dioxide and the breakdown of amino acids to urea. Energy is released in the process. **Anabolism** relates to the building up of more complex structures from simple ones, e.g., nitrogen is first converted to ammonia and then to complex organic nitrogen compounds, the formation of fatty acids from acetic acid and the formation of proteins from amino acids.

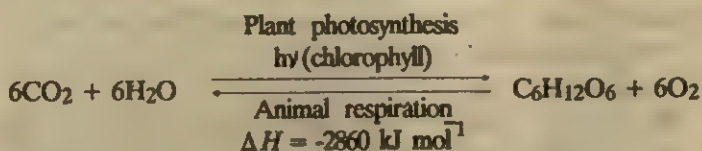
Yeast (a bacteria) also assists in breaking down (**anaerobically**, a catabolic process which takes place in the absence of oxygen) complex organic molecules, such as glucose into simpler molecules like ethanol, acetic acid or lactic acid. All these reactions take place with release of energy. A large portion of the energy released is stored as chemical energy in compounds such as nucleoside triphosphates. These compounds, in turn, react with water (hydrolysis) releasing energy. This energy is utilized by the cell for muscular contraction and locomotion, for initiating synthetic chemical reactions to produce structural and functional components of the cell, for carrying substances across membranes and to initiate the process of specific metabolic reaction sequences.

The complex molecules in a cell are polymers of very high molecular masses, e.g., carbohydrates, proteins, and nucleic acids. Proteins and carbohydrates are the two major constituents of our food intake. Proteins are found in all parts of the body and help in the maintenance of body in many ways. Some proteins are structural components of skin, muscle, and hair. Others control the transmission of nerve impulses. Some of the proteins work as enzymes or biocatalysts which accelerate many reactions in cells. The deoxyribonucleic acid, DNA, is the organic molecule in which an organism collects information about its genetic characteristics which, in turn, is transmitted from generation to generation. Carbohydrates serve as store house of energy and structural material of plants.

19.3 CARBOHYDRATES

This class of compounds are among the most major constituents of most living systems; act as the main source of energy for biological processes as well as a structural component in plants. In plants, they form the greater part of the cell tissue on which the plant relies for its support. They include familiar substances like glucose, sucrose, starch, cellulose, etc. They provide with all the three basic needs of life, viz., food (as starch containing grains) clothing and shelter (cellulose in the form of cotton, linen, wood, etc.). The name originates from the fact that many sugars (which form parts of this class of compounds) have the general formula $C_n(H_2O)_m$ - i.e., carbon hydrate- hence, the name carbohydrates. Thus, glucose, $C_6H_{12}O_6$ the most common sugar, can be written as $C_6(H_2O)_6$ and sucrose as $C_{12}(H_2O)_{11}$. However, these representations do not explain their relative nature. They bear little or no relationship to the structures known today.

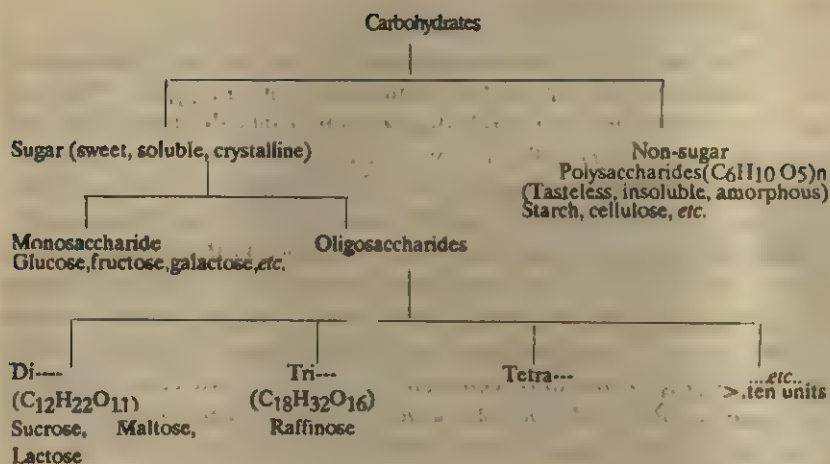
They are produced by green plants (by chlorophyll, the green pigment of plants) in nature from carbon dioxide and water by the action of sunlight *via* a process called photosynthesis. Thus, carbohydrates are the end products of photosynthesis in plants.



The driving force for the reaction is supplied by sunlight. This reaction helps in storing some of the energy given out by the sun. Animals consume the carbohydrates and convert them back to carbon dioxide and water, in the process releasing and using the stored energy of the sunlight.

19.3.1 Classification

Carbohydrates are grouped into two main classes: the sugars and the non-sugars (polysaccharides). Further sugars are classified according to the number of basic sugar units present in their structure. Glucose is one of the basic units of more complex sugars and as such is known as monosaccharide. Combination of several such units are known as di-, tri, tetrasaccharides, polysaccharides.



In terms of their functional groups, carbohydrates are polyhydroxy aldehydes (e.g., glucose), polyhydroxy ketones (e.g., fructose), or molecules which yield polyhydroxy aldehydes and ketones on hydrolysis. Sugars containing an aldehyde group are collectively called 'aldoses', while the ketonic sugars are referred to as 'ketoses'. Thus, glucose is referred to as an aldohexose while fructose is an example of ketohexose (both glucose and fructose contain six carbon atoms and individual sugars end in the suffix - 'ose', hence, the name hexose).

19.3.2. Monosaccharides

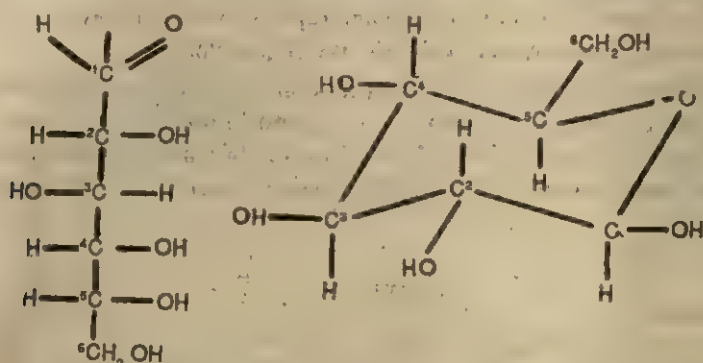
These are the simplest sugars which do not hydrolyse. There are about twenty monosaccharides which occur naturally. They are classified according to the carbons, as trioses, tetroses, pentoses, hexoses and so on (Table 19.3). They are highly soluble in water, decompose on heating and have a sweet taste. They are colourless and crystalline compounds.

Table 19.3 Monosaccharides

Class	Molecular formula	Example
Trioses	C ₃ H ₆ O ₃	Glycerose
Tetroses	C ₄ H ₈ O ₄	Erythrose
Pentoses	C ₅ H ₁₀ O ₅	Ribose
Hexoses	C ₆ H ₁₂ O ₆	Glucose, Fructose.

The trioses are obtained as one of the products during the course of metabolic breakdown of the hexoses. Ribose, glucose and fructose are the important monosaccharides. The ribose (C₅ sugar) is an important chemical component of the nucleic acids.

1 Glucose, the most important monosaccharide can exist as a straight chain or cyclic molecule. The first clue of the existence of cyclic conformation of each d-glucose and l-glucose came with the change in rotation



(I) Open chain structure (Glucose or Aldohexose) (ii) Cyclic

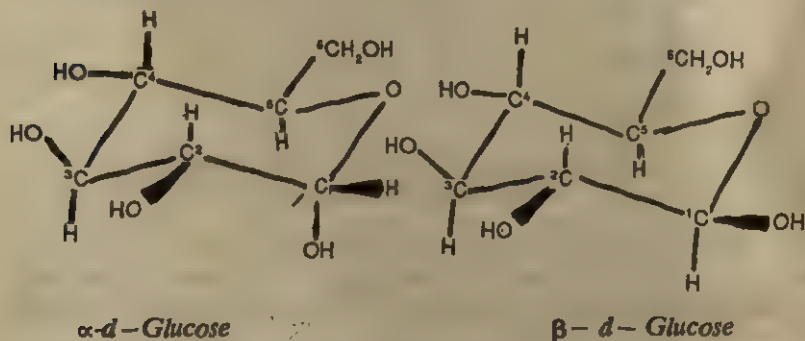
of freshly prepared solution of each forms (d-glucose + 112.2°; l-glucose + 18.7°) to a stable rotation of + 52.7°, a phenomenon termed **mutarotation**. In solution there is an equilibrium between the two types of structures.

A number of points emerge from the structures. Firstly there is a large number of hydroxyl groups. These, it is thought, are responsible for the sweet taste of sugars and are certainly responsible for their high solubility in water. In glucose (I), the hydroxyl groups at position 2,3,4,5 and 6 are, in fact, typical alcoholic groups; 6, being a primary alcohol group and the others secondary. Another point which emerges is that there are four asymmetric carbon (a carbon atom attached to four different atoms or groups is called asymmetric carbon atom and is said to possess a chiral centre) atoms in glucose (I), atoms 2,3,4 and 5 with a potential of 16 isomers (8 d l pairs). The projection of the -OH groups was correctly deduced by Emil Fischer. Out of sixteen possible aldohexose isomers, only d-glucose, d-mannose and d- and l - galactose have been isolated from natural sources, while the others have been synthesized.

Aldehyde and C-5 alcoholic groups interact to form a cyclic hemiacetal (II), thereby, producing a new asymmetric carbon atom and giving rise to two distereoisomers. The favoured conformation resembles the chair form of cyclohexane. Structurally α , and β forms are distinguished by the projection of hemiacetal - OH group (the C-1 OH group) which projects downward (axial) group in α - glucose and

upward (equatorial *i.e.*, extends out from the ring) in β glucose. This slight, structural difference of α and β forms is of high significance. Starch, a polymer of α - glucose units is digestible. However, the enzyme systems of man distinguish and reject cellulose, a polymer of β - glucose units, consequently, cellulose is indigestible.

Glucose is the most abundant naturally occurring monosaccharide. It occurs in plants and animals. It is found in honey, ripe grapes, and other sweet fruits and in the blood and urine of man. It is also found in saps of plants, blood, and tissue of animals. Depending on the source, it



has been called grape sugar, corn sugar and blood sugar. It is also called dextrose.

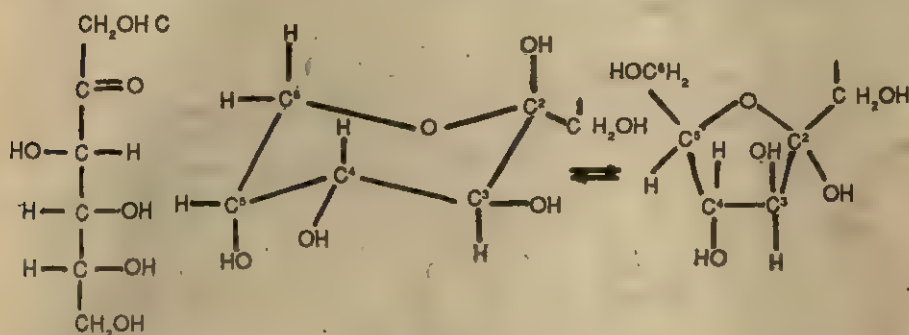
Human body normally contains about 0.1 percent of this sugar. Sometimes a solution of glucose is injected directly into the blood stream of patients seriously in need of nourishment, as it is the immediate source of energy for energy requiring cellular reactions in the body such as tissue repair, macromolecular synthesis, muscle movements, *etc.* An average adult has five to six grams of glucose in his blood. This can supply energy for about 15 minutes and is continuously replaced in the body.

Diabetic patient's body cannot assimilate glucose and this sugar is eliminated through the kidneys. The urine may contain as much as 8 to 10 percent of glucose in such cases, and its presence there is one symptom of the disease.

Glucose is the major structural component of some important higher saccharides such as sucrose, maltose and lactose.

Fructose, a monosaccharide, is the only ketohexose commonly encountered in biochemistry. It is the sweetest of all the monosaccharides. It can exist in both chair (pyranose) and ring (furanose) forms. It is the basic unit of insulin, a polysaccharide.

Fructose occurs in a large number of fruits and in honey. It can be converted to glucose in the liver and intestine, and hence, used in the body.



d - Fructose
(A ketohexose)

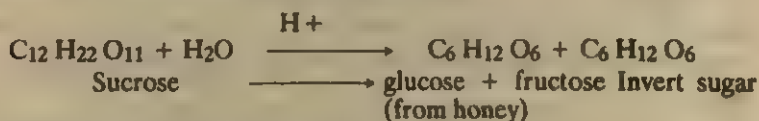
β - Fructopyranose

α - Fructofuranose

19.3.3 Oligosaccharides

These are built up of a certain number of monosaccharide units that are split on hydrolysis. Disaccharides and trisaccharides belong to this class.

In disaccharides, two simple sugar units are joined by the elimination of water between the aldehyde group of one sugar and hydroxyl or ketonic group of the other (the two monosaccharide residues need not be the same). This forms an acetal (double ether) linkage called a glycoside bond. They can be hydrolyzed by enzyme action or by boiling with dilute mineral acids to the constituent monosaccharides.

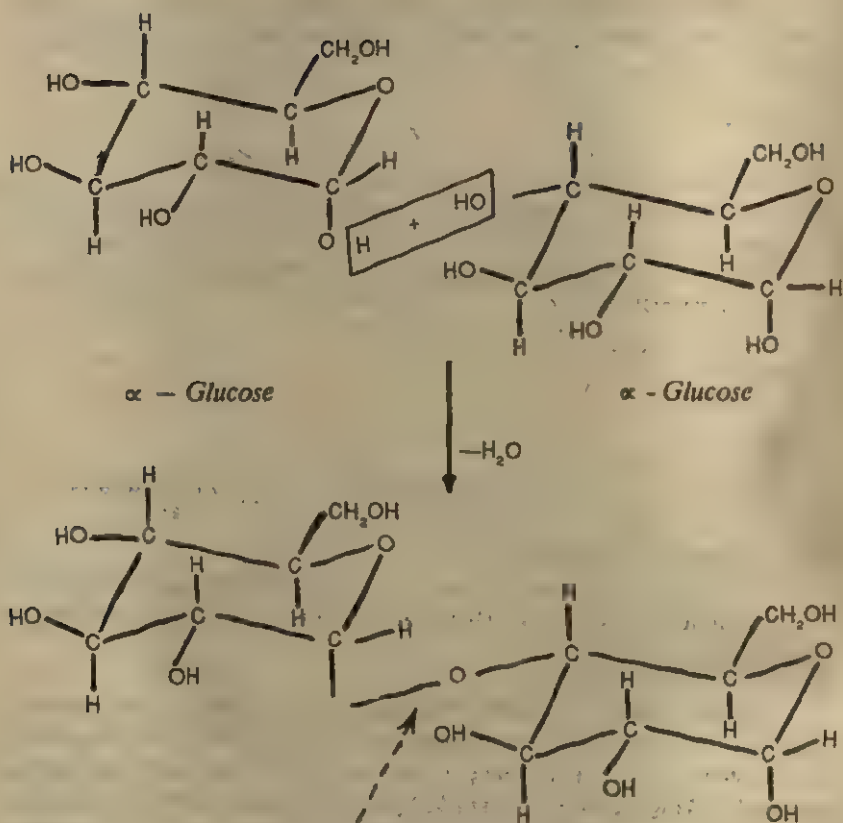


(Juice or sap of plants such as sugarcane, sugar beet, pine apple and carrot roots)

Maltose \longrightarrow glucose + glucose
(on enzymatic hydrolysis of starch)

Lactose \longrightarrow glucose + galactose
(milk sugar)

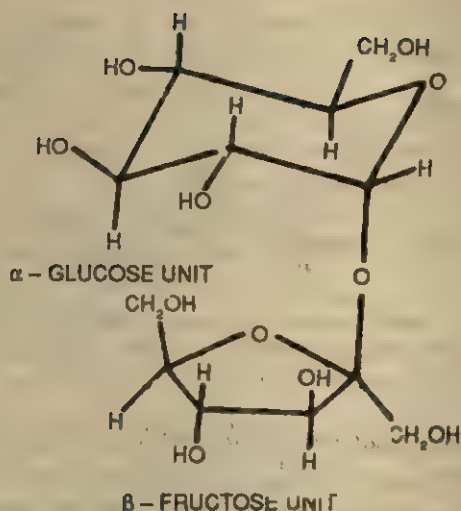
Sucrose is isolated from the juice or sap of several plants including sugar cane and sugar beet. Hydrolysis of sucrose by acid or by enzymes gives invert sugar - a mixture of equal molar quantities of glucose and



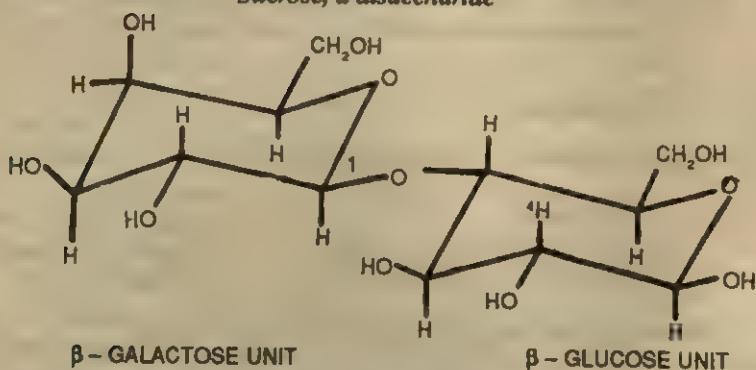
*Glycosidic linkage.
Maltose, a disaccharide*

fructose. Honey is a rich natural source of invert sugar. It is also produced on a industrial scale and used when non-crystalline sweetner is required.

Maltose or malt sugar contains two sugar units. It is formed by the action of an enzyme called 'diastase' upon starch or by the partial hydrolysis of starch or dextrins by dilute acids. Maltose is fermentable in the presence of yeast, since yeast produces both maltase, which catalyzes the conversion of maltose to glucose and zymase, which catalyzes alcoholic fermentation of glucose. Lactose occurs in the milk of cow to the extent of 5 percent. It occurs to about 7% in human's milk. Pure lactose is obtained from the watery byproduct of cheese production. Hydrolysis in the presence of either dilute mineral acid or lactase converts lactose and galactose (an isomer of glucose). Certain microorganisms catalyze the fermentation of lactose to butyric acid or lactic acid. These acids are responsible for the souring of milk. Lactose is a whole some food of infants.



Sucrose, a disaccharide



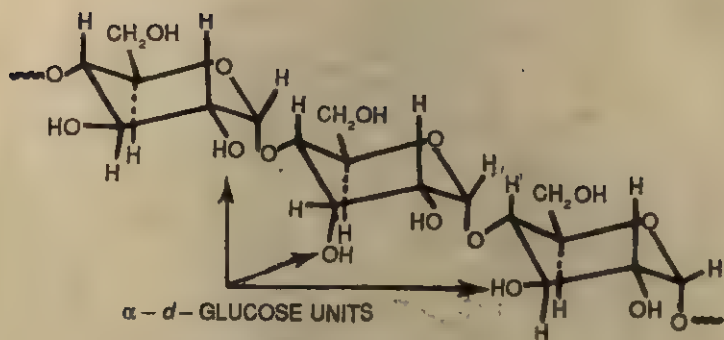
Lactose, a disaccharide

19.3.4 Polysaccharides

The repeated condensation polymerization of monosaccharide units leads to the formation of a polysaccharide molecule. Individual sugar units may be connected to one another to form linear, branched, or circular polysaccharides.

Starch is a polymer which is made of α -glucose units only. It is the major storage form of glucose in plants. It is accumulated by plants in seeds, tubers and fruits. It is often the major food supply for the young plant until it has developed a leaf system and can manufacture its own food. It is an essential food source of carbohydrate and is found in cereals, potatoes, legumes, and other vegetables.

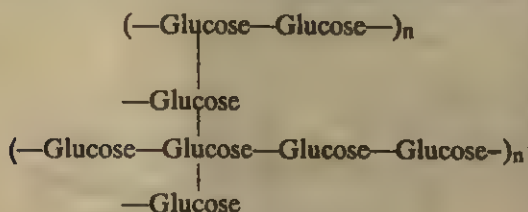
Cellulose is the material of plant cells, as in wood. Cotton contains about 80 percent pure cellulose. Like starch, cellulose is a polymer of



A portion of starch molecule; Starch, a polysaccharide

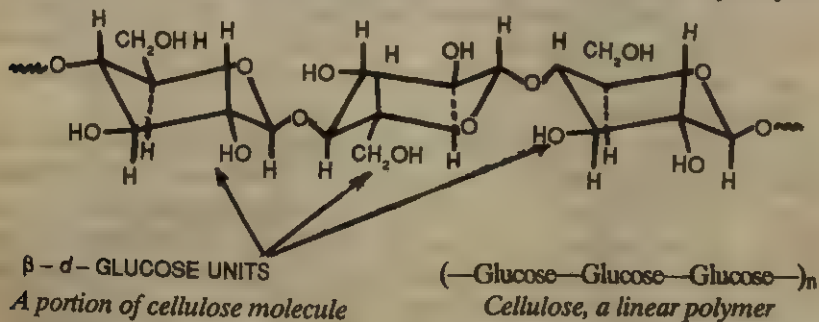
β -glucose joined together through oxygen linkages to form long chains. The use of α -glucose in starch and that of β -glucose in cellulose is of

high significance. It affects the chemical structure and properties of starch and cellulose. Cellulose is a linear polymer and mechanically much stronger than starch which is a branched polymer.



Starch, a Branched Polymer

Human beings can convert starch to its fuel form, glucose, but they lack enzymes to catalyze the hydrolysis of cellulose to glucose. Animals such as cows, sheep, goats and deer have intestinal bacteria that produce enzymes for breaking down cellulose into glucose. These animals can, therefore, use cellulose as a nutritional source. They can be hydrolyzed



Cellulose, a polysaccharide

by the action of enzymes or mineral acids to monosaccharides. They are difficult to hydrolyze as compared to disaccharides and intermediate products can be isolated during the course of the reaction.

Starch, glycogen and cellulose (about 3000 glucose units) are macromolecules, high molecular mass polysaccharides consisting of glucose units linked by glycoside bonds. Their size place them in the colloids category. They are insoluble, but disperse in aqueous media as typical colloids. These do not possess reducing properties as potential aldehyde groups are destroyed by glycosidic linkages.

19.3.5 Preparation of Glucose

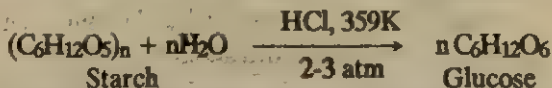
Glucose is the most important monosaccharide (aldohexose) since starch and cellulose, etc. are built of glucose units. It is also called dextrose due to its optical rotation or grape sugar. Glucose is the blood sugar of man. It is widely used under the label 5% dextrose for intravenous feeding, since it requires no digestion. Glucose is a threshold metabolite, one that is selectively reabsorbed in the renal tubules.

From sucrose : Glucose is prepared by the hydrolysis of sucrose (a cane sugar), which on boiling with dilute hydrochloric acid or sulphuric acid in alcoholic solution gives glucose and fructose. On cooling the solution, glucose being almost insoluble in alcohol separates out in the crystalline form.

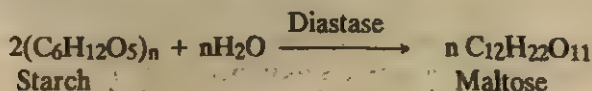


If sucrose, present in molasses (obtained during sugar refining) is used, yeast is added for hydrolysis. Yeast contains an organic catalyst or enzyme known as invertase that causes the sucrose to be hydrolyzed to two sugar units glucose and fructose. But these sugars are converted to alcohol by zymase present in yeast.

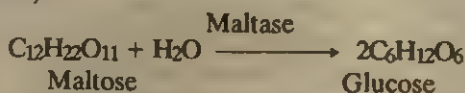
From starch : (I) Commercially, glucose is obtained by the incomplete hydrolysis of starch by heating with dilute HCl or H₂SO₄ at 395K under a pressure of 2–3 atm. The resulting solution is neutralized with CaCO₃ and the calcium salts are filtered off. The filtrate is decomposed by boiling with animal charcoal and concentrated under reduced pressure.



(II) Starch, extracted from raw materials such as wheat, potatoes, barley or rice by using superheated steam, is treated with malt. Malt contains the enzyme diastase which helps the starch to be hydrolyzed to the sugar maltose.



Yeast is now added and the enzyme maltase in yeast converts the maltose to glucose,



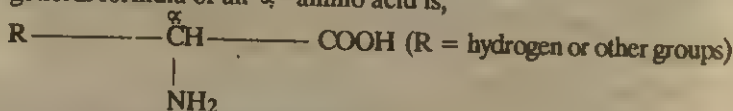
but the enzyme zymase present in yeast converts glucose to ethanol and carbon dioxide.

Glucose may also be obtained by the hydrolysis of cellulose.

Note : The hydrolysis of the starch present in the food material begins in our mouth catalyzed by the enzyme, amylase (present in saliva). When the starch reaches the stomach the dilute HCl present there catalyzes the hydrolysis to glucose.

19.4 PROTEINS

Proteins in life provide protection as skin, hair and nails and motive power as muscles. As enzymes, they sustain life by speeding up otherwise slow chemical reactions. Thousands of different types of proteins go into the make up of a living cell. They take part in thousands of chemical reactions that occur in a living cell. Proteins are gigantic polymeric macromolecules of amino acids with high molecular mass produced in plants and animals. They are considered to be the building units of all vegetable and animal bodies. Proteins are essential part of diet and are vital for the maintenance and growth of life. The name protein is derived from the Greek word 'proteios' meaning first or primary, i.e., compounds of primary importance. They contain the elements carbon, hydrogen, nitrogen, oxygen and sometimes sulphur and phosphorus. Proteins are built of long linear chains of some 20 different α -amino carboxylic acids. The general formula of an α -amino acid is,



Their complexity is associated with the unique structural characteristics of interactions of amino acids. The way all the words of the English language are given by combination of the characters of the alphabet, the proteins of all living organism with their diverse functions are derived from the 20 amino acids.

Proteins perform a wide variety of biological functions. Some of the important proteins and their functions are given in Table. 19.4

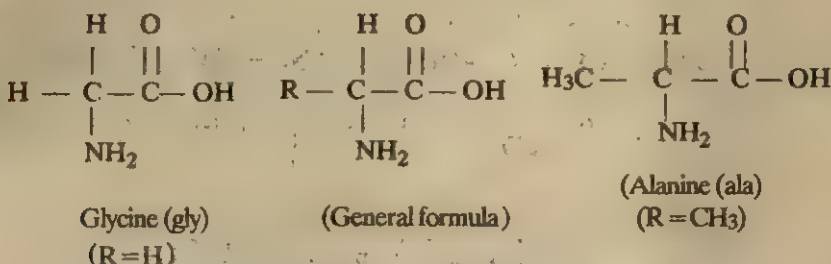
19.4.1 Amino acids

Studies of the products obtained on protein hydrolysis show that proteins are made up mainly of just twenty naturally occurring amino acids. Although there are structural differences among the common amino acids, there are also certain similarities. They all contain an amino and a carboxyl groups attached to the same carbon atom and are designated α -amino acids. Further, α -carbon atom is asymmetrically

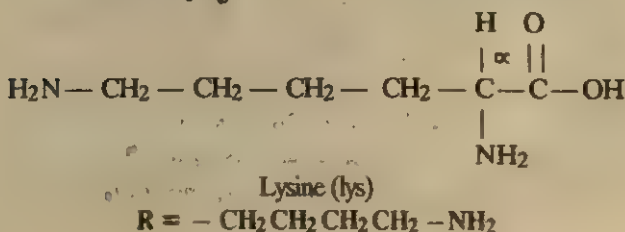
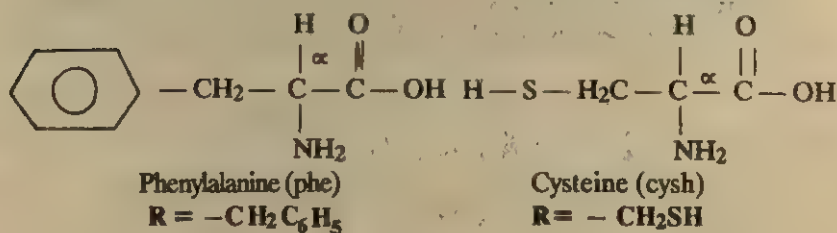
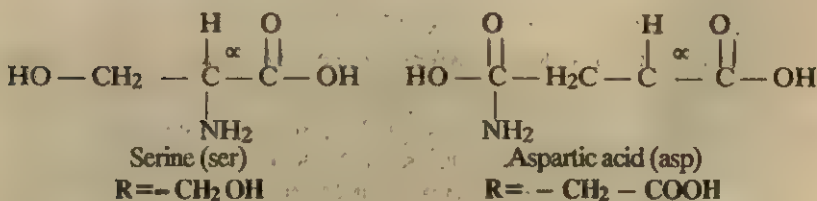
TABLE 19.4 Biological functions of some important proteins.

Type	Examples	Function
Enzymes	Trypsin, Pepsin	Catalyzes some of the biochemical reactions
Information transmission	Insulin, Glucogen	Hormones
Motion	Myosin, Actin	Helps in muscle movement
Storage	Myoglobin	Stores oxygen in muscles until it is required for energy production.
Structural	Collagen, Keratin	Structural and protective function occurs in hair, nails, teeth, etc.
Transport		Carries oxygen from lungs to various tissues through blood stream.

substituted in all cases except glycine. They all differ in the chemical nature of side chain R,



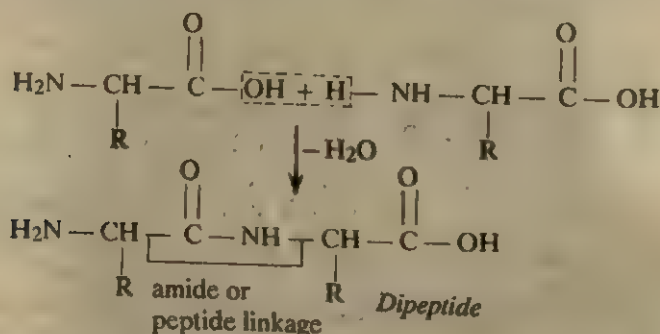
Some amino acids with different side chains are given below:



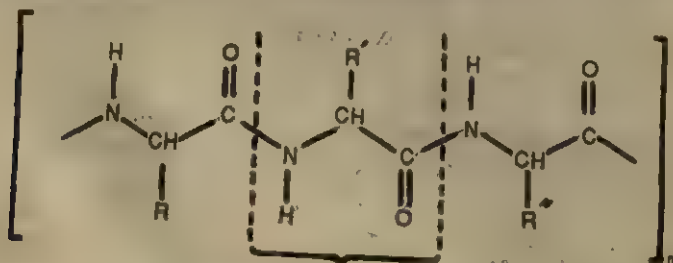
The nature of side chain is important in determining the properties of the resulting proteins. All amino acids have a basic group ($-\text{NH}_2$) and acidic group ($-\text{COOH}$) which can react with each other or with other sources of acid or base. The most important reaction of amino acids is that involving amide formation.

19.4.2 Peptide Bond

Amino acids units are linked together by condensation reaction involving the loss of a water molecule between each joined unit. The α -carboxyl group of amino acid and the α -amino group of another join through amide linkage, called peptide linkage. The resulting structures are called peptides.



Depending on the number of amino acid residues per molecules, they are referred to as dipeptides, tripeptides and so on finally polypeptides. A protein molecule is a polypeptide and may contain hundreds or thousands of amino acid units joined in a linear fashion. Their molecular masses range from 15000 to 60000 amu or more. The polypeptide chain in proteins forms the backbone of primary structure of polypeptides. Proteins may be represented by the following formula :



*A unit of the polypeptide
Formula for primary polypeptide structure*

The amide linkage (peptide linkage) is essentially planar, since the nitrogen orbital containing a lone pair of electrons overlaps with the carbonyl π electrons, and the electron density is spread over the O—C—N atoms (Fig. 19.3) This type of overlap imposes a barrier to rotation about the carbonyl C—N bond. Protein chains, however, can twist, curl or entwine because of the asymmetric carbon atom between the nitrogen atom and carbonyl carbon atom (Fig. 19.4). These discoveries have been made through the application of X-ray diffraction techniques; much of the credit for this very important work goes to Linus Pauling who received the Nobel Award in 1954.

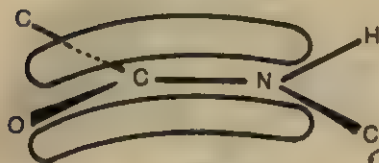


Fig. 19.3 Amide : Lone pair overlap with π electrons

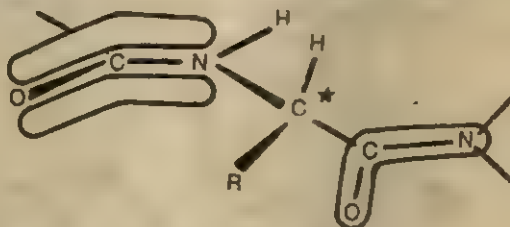


Fig. 19.4 Twisting of protein chain

19.4.3 Structure of Proteins

The basic chemical structure of proteins was determined by the German chemist, Emil Fischer between 1900-1910. Through his studies he established the presence of peptide bonds. Protein molecules differ among one another not only in the number and kind of amino acid residues but also in the order in which the residues are arranged in the polypeptide chains. This means that the number of possible protein structures is very large. Each protein has a distinct order of arrangement of the amino acids in the peptide chain. This order of arrangement is called the **primary structure** of the protein. Frederick Sanger, a British chemist, in 1953, elucidated the primary structure of protein hormone **insulin** for the first time. He determined the primary structure of beef insulin and for this work he was awarded a Nobel Prize in 1958. It has 51 amino acids that are joined through two polypeptide chains held together by S-S bonds. Since then, the primary structures of several hundred proteins have been studied and duly established. Primary structure, as we know, is the backbone of proteins. Change of one amino acid in the sequence can disrupt the biological activity of the protein. For example, in **haemoglobin** - the protein present in blood which is a carrier of oxygen - replacement of one particular amino acid makes it defective for our purpose. This causes a disease called sickle cell anaemia. In patients, suffering from this disease, the defective haemoglobin in red blood cells precipitates causing the cells to sickle and sometimes burst.

Polypeptide chains are quite flexible and can take on many different shapes. Polypeptide chains tend to form random coils or adopt helical or sheet structures. These arrangements are termed as the **secondary structures**. This has been possible because the flexible polypeptide chains could be stabilized by hydrogen bonds, extending from the hydrogen attached to the nitrogen of one amide group to the carbonyl oxygen of another amide group. Two types of shapes that occur frequently in proteins are the α -helix, similar to a cork screw, (Fig. 19.5, because of intramolecular association within a chain), a spiral arrangement of the polypeptide chain and the β -structure (Fig. 19.6 -intermolecular hydrogen bonding between two different polypeptide chains), an arrangement of pleated sheet.

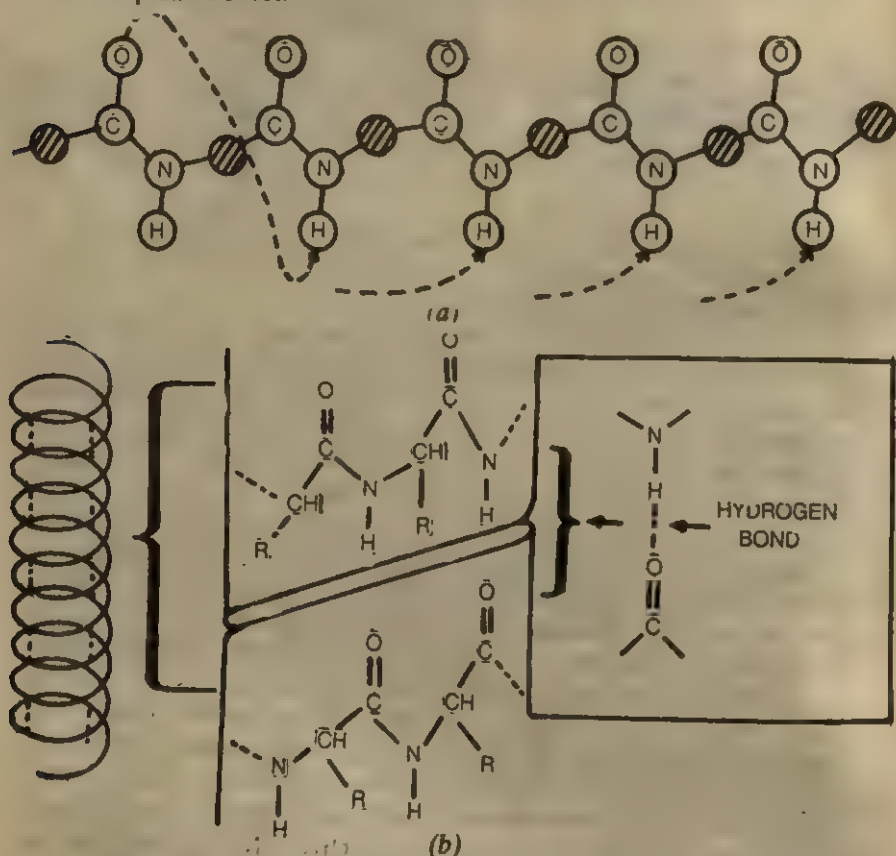


Fig. 19.5 Structure of α -helix in proteins: (a) linear polypeptide chain. The dotted lines show the centres of hydrogen bonding within the same chain between the different amino acid residues, (b) Polypeptide chains tend to coil in a form called an α -helix. This coiling produces a three dimensional tubular aspect to the protein chains. As shown hydrogen bonds tend to hold the α -helix in place.

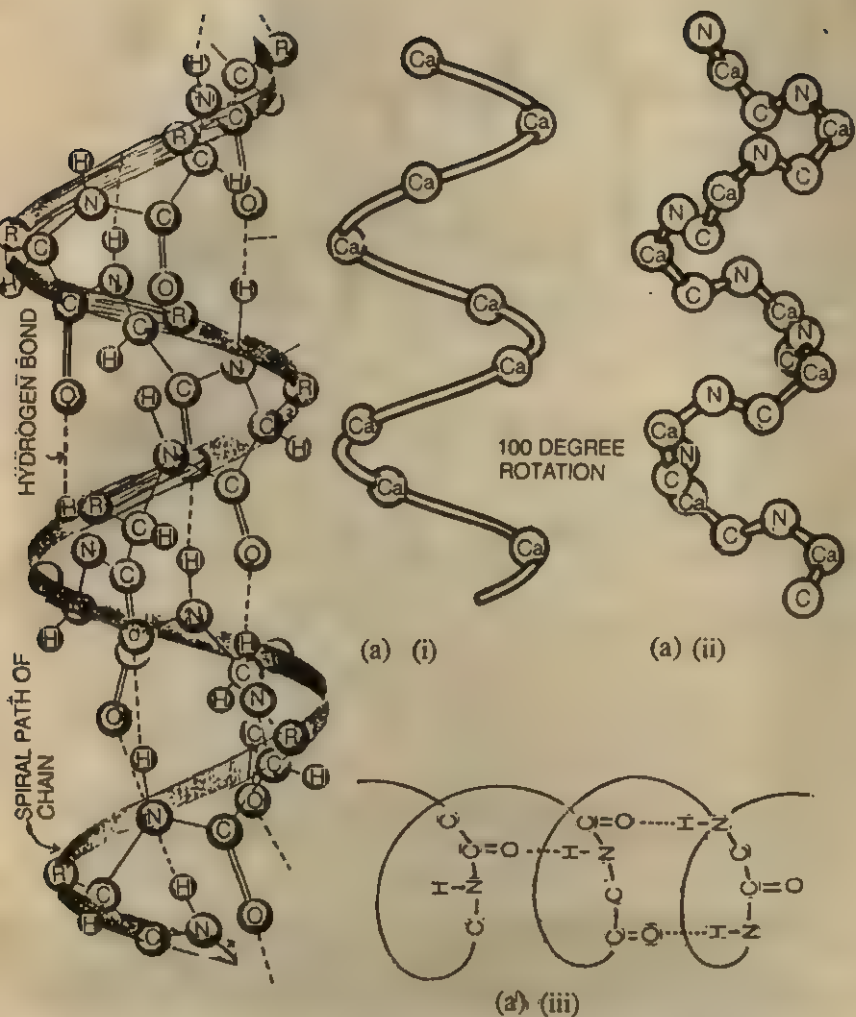
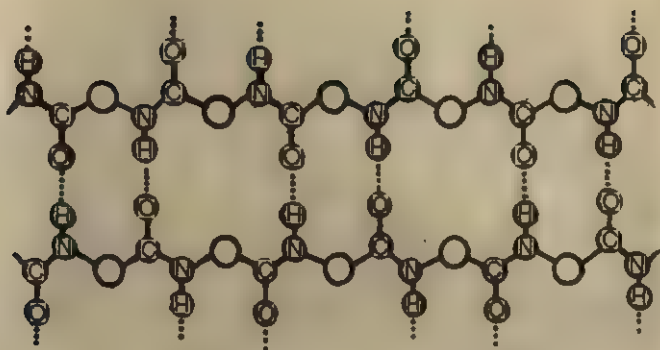


Fig. 19.5 Structure of α - helix in proteins (c) intramolecular hydrogen bonding in α - helix of a protein with 3.6 amino acid residues per turn. The helix is stabilized by the linkage of NH and CO of peptide bonds by hydrogen bonds. (d) the Polypeptide backbone. The dotted lines show the hydrogen bonds between the carbonyl oxygen of one amino acid residue and the N-H hydrogen of the fourth residue

In the polypeptide backbone of the alpha helix there are 3.6 amino acid residues for each turn of the helix link. Each amino acid residue forms a hydrogen bond through its carbonyl oxygen with the N-H hydrogen of the fourth residue. Although hydrogen bonds are weak, the



Intermolecular hydrogen bonding between two parallel polypeptide chains



Fig. 19.6(a) Intermolecular hydrogen bonding between two parallel polypeptide chains leads to formation of sheet structures, (b) schematic picture of beta pleated sheet.

cumulative effect of several hundred hydrogen bonds in a protein molecule is enough to ensure structural integrity. This type of integrity is imperative to the biological functions of the protein and if it is irreversibly destroyed the protein can no longer function.

The beta pleated sheet consists of peptide chain arranged side by side to form a structure that resembles a piece of paper folded into many pleats. The carbonyl groups of one peptide chain are hydrogen bonded to N-H hydrogens of adjacent peptide chain that run in opposite direction so that the N-terminal of one get oriented against the C-terminal of other. In fact, a number of such chains can be interbonded together to form sheet. Such sheets tend to stack one upon another to form three dimensional structure called a beta pleated sheet. Beta pleated sheets are formed by separate strands of protein or by a single chain looping back

on itself. Silk possess structure of this nature with the protein chains running in the direction of silk fibres. This arrangement imparts to silk its characteristic mechanical properties. Silk fibre is not elastic. On stretching, the covalent linkages are destroyed. On the other hand, silk fibres can bend easily because its protein sheets can slide over each other. Silk (fibroin), wool, (keratin) and hair (collagen) are the examples of fibrous proteins. The proteins present in stretched hair and muscle and wool have been shown by x-ray analysis to possess polypeptide chains arranged in parallel fashion forming sheets (Fig.19.6). They tend to be long, rod shaped molecules with great mechanical strength. These proteins possess elastic nature. On stretching, the weak hydrogen bonds are broken, and thus, tend to increase in length like a spring. On releasing the tension, the hydrogen bonds are reformed and thus, help the protein molecules to acquire their original shape.

Tertiary Structure of Proteins

A third structural modification of proteins called tertiary is found in the non-stretch connective tissues in ligaments and in the strengthening networks of skin. It has been established with the help of X-ray studies by Kendrew and Perutz (Nobel Award 1963) that both the helical and non-helical regions of the peptide chain are present in this type of protein. These helical pleated sheets may be additionally folded or twisted into three dimensional space in a highly specific manner. These specific tertiary structures can interact with each other to form more complex molecules. The secondary and tertiary structures are an outgrowth of the primary structure of a protein. Myoglobin present in muscle and haemoglobin found in blood belong to this class. These proteins are called globular proteins and possess more or less spherical shape (Fig. 19.7)

The tertiary structure of a protein is controlled by several different kinds of interactions (Fig. 19.8) that serve to hold the folded segments of the chain in place. For example, besides hydrogen bonding, there exist ionic attractions that occur between a negatively charged deprotonated carboxyl group and a positively charged protonated amine group.

The portions of protein that cannot be described as either α - helix or β - structure are called random coils. A typical protein may contain portions of each of the three different classes of three dimensional arrangements.

The random coil parts of a polypeptide chain and weak sites in its α - helixes and β - structures impart too much flexibility to the chain. Interactions between side chains fold the polypeptide chains into convoluted shapes (the tertiary structural characteristics).

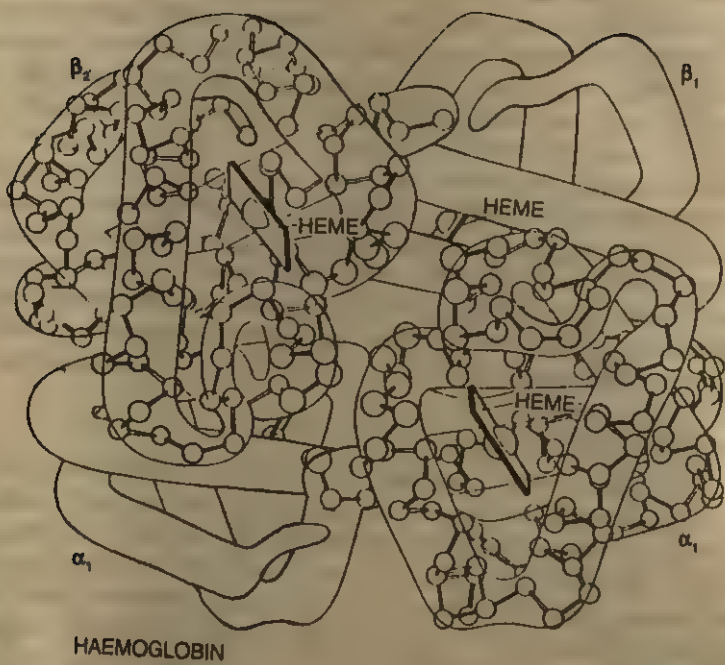


Fig. 19.7 (a) Haemoglobin (b) Myoglobin

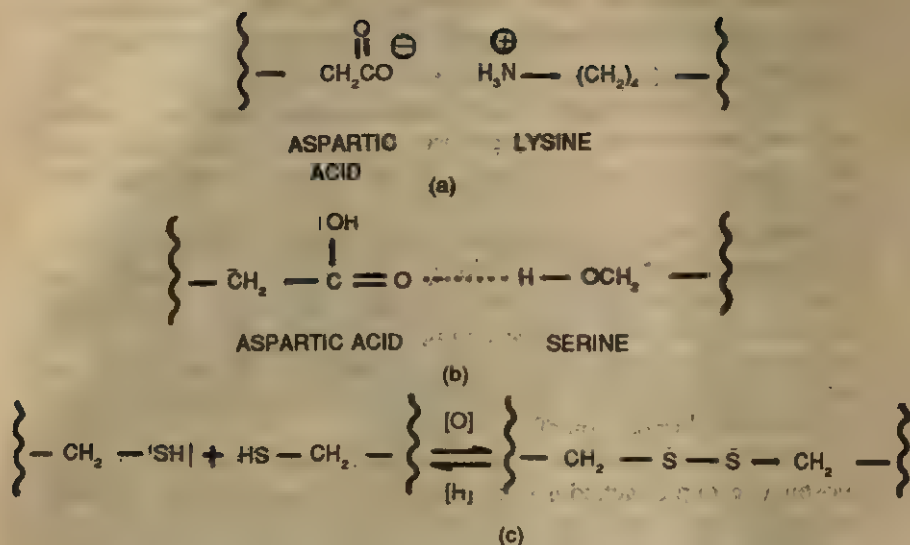


Fig. 19.8 Linkages contributing to the tertiary structure of proteins
 (a) Salt linkages : Acid-base interactions between different coils; aspartic acid unit donates a proton to the free amine group of a lysine unit (on different coil), (b) Hydrogen bonding : Interactions between side chains of certain amino acids, and (c) Disulphide linkages : Oxidation of the highly reactive thioalcohol (-SH) group of cysteine to a disulphide (-S-S-) can occur.

19.4.4 Chemical Characteristics of Proteins

Protein molecules tend to unfold and lose their characteristic shapes when exposed to heat, extreme pH or non-aqueous solvents. These reactions called 'denaturations' change the physical properties of proteins and destroy their biological activity. Coagulation of egg albumin (white of an egg) by heat is a familiar example of denaturation. Concentrated acids, bases, strong electrolytes and heavy metal ions (Hg^{2+} , Hg_2^{2+} , Ag^+ , etc.) also help in denaturation.

Amide links of proteins are readily hydrolyzed: a protein therefore, can be broken down to give a mixture of different α - amino acids. The mixture can be analyzed for the relative amounts of different amino acids in the protein by chromatography technique. Further it can be found which amino acid is at the amino end of a protein and which is at the carboxylic acid end of the molecule by appropriate reactions.

A long polypeptide chain can be broken up into smaller polypeptide fragments by specific enzymes which cleave amide bonds between specific pairs of amino acids. The terminal groups of these smaller polypeptide parts can, thus be ascertained. With the help of these

hydrolysis reactions and using careful logic, it is possible to determine the complete sequences of the amino acid units in a protein molecule.

Classification of Proteins

In our discussions, we came across proteins which on hydrolysis yield only amino acids : the simple proteins. A second class of proteins, the conjugated proteins, yield, on hydrolysis, substances other than amino acids.

Simple proteins: (a) Albumins - from blood serum and egg white, (b) Globulins - from blood serum, (c) Glutelins - from cereal grains: wheat, corn and barley, (d) Scleroproteins - such as the elastin of connective tissue, the keratin of hair, horn, hoofs, and feathers, and collagen, the most abundant animal protein (e) protamines - low molecular mass basic proteins usually associated with nucleic acids, (f) Histones - such as globin, the protein portion of haemoglobin,

Conjugated Proteins : (a) Phosphoproteins - with one or more phosphate group attached usually to the -OH group of a serine molecule, such as pepsin, found in the stomach, (b) Lipoproteins - with a lipid unit bonded in some fashion to the protein; approximately 70% of the lipid found in blood plasma is bound to protein, (c) Mucoproteins - with large amounts of carbohydrates, (d) Glycoproteins - with small (~4%) amounts of bound carbohydrate (e) Chromoproteins - with a group attached affording a visible colour, including haemoglobin and other respiratory pigments.

Proteins can be divided into two main classes on the basis of their structural features: (i) **Fibrous proteins :** These are insoluble in water. These proteins have long thread like molecules. Hairs, nails, hoofs, muscle proteins are examples of fibrous proteins (ii) **Globular proteins :** These are soluble in water and in aqueous solutions of salts, acids and bases. The molecules of globular proteins appear as globules, i.e., have an almost spherical shape. These proteins are of vital importance to living systems, because these act as catalysts for many chemical reactions occurring in the cells.

19.4.5 Enzymes

Most of the life giving chemical reactions that occur in your body (and the bodies of all other living things) involve complex organic molecules, e.g., carbohydrates and proteins. As you already know (Section 19.1) that reactions between organic compounds are mostly slow. Without very effective catalysts, most of the reactions, (hydrolysis of proteins, etc.) that give you energy to live would take place at a rate far too slow to sustain life. Such catalysts are called enzymes. Enzymes themselves are globular proteins that serve to catalyze chemical reactions in living systems. Thus, an enzyme is a complex protein molecule

produced by a living cell that catalyzes a reaction of the cell. It has a very specific catalytic function. For example, the manufacture of alcohol from sugars by fermentation is catalyzed by the enzyme, zymase which is produced by yeast cells (Section 19.3.5).

A typical cell contains about 3000 different kinds of enzymes. Unlike many reactions in a laboratory, most of the biochemical reactions in cells take place in aqueous solutions (a cell contains about 70 percent water) at pH 7.0, at physiological temperatures (37°C or 310 K) and at atmospheric pressure. Under these conditions, these reactions are not likely to take place at a significant rate without taking the help of enzymes. So, to some extent your existence is because of enzymes you have. Your genes determine the enzymes your body has the ability to synthesize. This ability of producing enzymes is passed from generation to another generation.

A human body with a genetic defect (absence of an enzyme) does not function effectively. In some case, an enzyme deficiency is caused by the dietary deficiency. For example, vitamins are needed to synthesize certain enzymes. Long absence of a particular vitamin in your food can cause disease and even death. Thus, the symptoms of the vitamin deficiency may be correlated to the deficiency of certain enzymes.

Mentally retarded children suffer from a disease known as phenyl ketone urea. This is caused by the deficiency of the enzyme phenylalanine hydroxylase.

Some enzymes require an additional substance called a coenzyme to function effectively. Many vitamins that you normally consume to maintain good health are precursors of coenzymes. Vitamin B_{12} , whose deficiency in the diet causes a disease known as pernicious anemia, is changed into its coenzyme in the body. Many metals, like cobalt, etc. are essential (in small amount) to enhance the activity of enzyme.

Enzymes have the following characteristics:

1. Remain unchanged during the course of reaction
2. Do not change the normal position of chemical equilibrium
3. Act as a catalyst for a specific chemical reaction – specificity
4. Act efficiently – the rate of some reactions is increased several hundred thousand fold (10^{20}) in the presence of an enzyme.

The last two properties are very remarkable. Many enzymes apparently catalyze only one reaction of the many thousands taking place all the time in the body. This is despite the fact that in some cases the compounds involved in different reactions may be similar. For example, the enzymes that catalyze the digestion of starch cannot catalyze the hydrolysis of cellulose. The following reaction will convey about the efficiency and specificity of enzymes. An enzyme carbonic anhydrase

present in the red cells of blood catalyzes only one reversible reaction, i.e., the breaking of carbonic acid into water and carbon dioxide.



In ideal conditions, i.e., in a perfect body, a single molecule of carbonic anhydrase can help in the breakdown of about 36 million molecules of carbonic acid in one minute. Ptyalin in saliva breaks down the starch like molecules in our food, and thus, helps in the growth of our body. Pepsin is another important enzyme which converts protein to simpler molecules.

The catalytic activity of an enzyme seems to be the greatest of all catalysts. The mode of its action is the same as that of any other catalyst, i.e., it increases the rate of reaction by lowering the energy of activation for the reaction or process (Fig. 19.9)

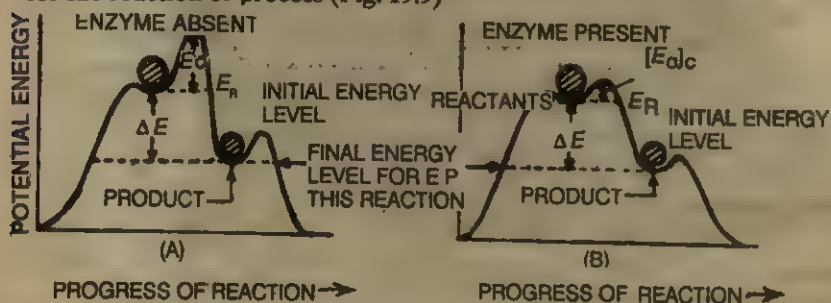
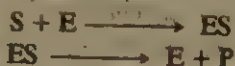


Fig. 19.9 The effect of enzyme on the activation energy

The plausible mechanism of enzyme action involves a reactant species called the substrate (S). It attacks the active site on the enzyme (E) and forms a complex (ES). In due course, the complex decomposes to produce a product species (P) and the original enzyme (E). Thus, a two step mechanism is :



The binding site is apparently quite specific and can bind only one or only one kind of substrate molecule. The specificity has been compared to a lock and key (Fig. 19.10).

In all such enzymatic reactions, the first step is reversible followed by an irreversible step. The reaction rate increases with the concentration of substrate until a stage is reached when further addition of substrate does not affect the rate. Enzyme activity is also affected by temperature at p^H .

19.5 NUCLEIC ACIDS

No area of scientific enquiry in the 20th century has generated more interest and speculation than the study of nucleic acids.

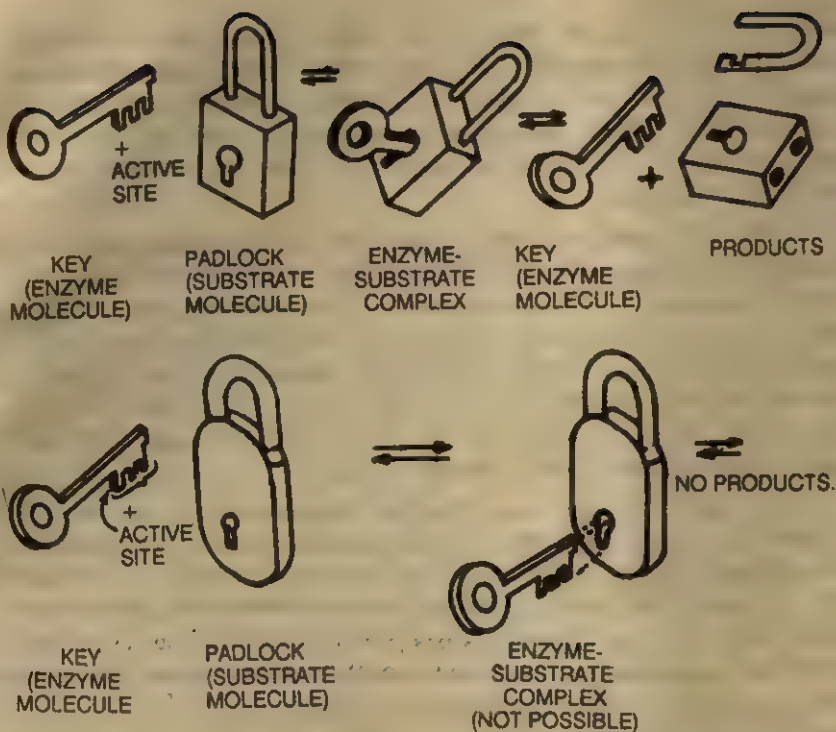


Fig. 19.10 The lock and key type relationship for the interaction of substrate and enzyme; (a) enzyme is effective (b) enzyme is ineffective.

One of the most mysterious aspects of life is the ability of living organisms to reproduce themselves. The fact that organisms are involved in reproducing their own species, continue to keep busy the chemists world over. **This reproduction is the self duplication of a cell by a division.** For a cell to live for ever, it is necessary that it must have a record of amino acid sequences, enzymes and proteins as they are the raw materials for the production of new cells and to repair damaged cells. From, different proteins different types of species will emerge. Thus, when a cell gets subdivided into two new cells, it is desired that they are equipped with identical information about their proteins.

How is this genetic information stored and transmitted within an organism (cell), and between parent and off spring ? This basic question of life and the mechanism of heredity has been the most challenging problems facing science today. This problem has been partly solved by the determination of the molecular structure of nucleic acids. Nucleic acids are the important constituent of the nuclei of all living cells. The nucleic acid macromolecules are of two major types: deoxyribose nucleic

acids (DNA) and ribose nucleic acids (RNA). DNA is found in the nucleus of the cell while RNA is found in the cellular fluid outside the nucleus, the cytoplasm. Both are found bonded to proteins as nucleoproteins. They are, however, chemically quite distinct from proteins and are made of nucleic acid units. Both are essential for the biosynthesis of proteins.

Within the nucleus there are giant nucleoprotein molecules that biologists call chromosomes. DNA constitutes parts of the chromosomes. Specific sequences of arrangement of the DNA groups on the chromosome are called genes. Genes determine all aspects of your body, structure and functions. They exercise their superiority at least in part by determining what enzymes your cells can produce. Chromosomes and genes occur in pairs. You inherited one gene of each pair from one parent and one from the other parent.

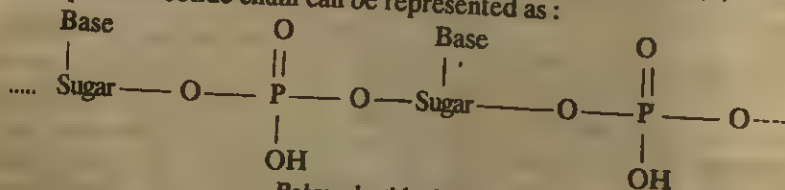
Nucleic acids make up less than one percent of the organic compounds present in the cells of living organisms; yet these compounds are imperative to life. They control all the chemical reactions of the cell and are responsible for the reproduction and transmission of hereditary information. Thus, nucleic acids carry genetic information as a chemical code that is passed on from one cell to another as they divide, and from one generation to another as organisms reproduce.

19.5.1 Structure of Nucleic Acids

Nucleic acids are polymers of simple structures called nucleotides. Partial hydrolysis of a nucleotide gives one molecule of phosphoric acid, one molecule of a five carbon sugar and one nitrogen base group. There are four types of base residues present in DNA. Two of these bases - thymine (T) and cytosine (C) are known as **pyrimidine bases**. The other two, adenine (A) and guanine (G) belong to the class of **purine bases**. Thymine which occurs in nucleic acids of the cell's nucleus is replaced by uracil in nucleic acids outside the nucleus in the cytoplasm.

RNA differs from DNA in two ways. (a) The sugar residue in RNA is a ribose whereas in DNA it is 2-deoxyribose, and (b) RNA contains pyrimidine base uracil (U) whereas DNA contains thymine (T).

A polynucleotide chain can be represented as :



Polynucleotide chain
(Base = Purine or pyrimidine)

The nucleotide units of DNA and RNA molecules have the purine and pyrimidine bases attached to the deoxyribose or ribose molecules to

give nucleosides. Thus, the backbone of the nucleic acid is a polyester chain. The acid part of the ester is phosphoric acid, and the alcoholic part is a sugar. Each sugar is linked (at C-1 through a β - linkage) to one of the four heterocyclic bases. Thus the primary structure of nucleic acid refers to the sequence of base residues attached to the sugar phosphate backbone.

The DNA and RNA differ in their molecular mass, shape and biological functions. The proportions of the bases and their sequence also differ in different nucleic acids.

Watson and Crick (1953) on the basis of chemical and X-ray data proposed a structure of DNA called the secondary structure. DNA consists of two identical polynucleotide chains (or strands) coiled with their heads in opposite directions around the same axis to form a double helix (Figs.19.11 and 19.11a). The two strands (*i.e.*, polynucleotide chains) are right handed and have ten nucleotide residues per turn. They are held together by hydrogen bonding between bases, which occupy positions at right angles to the axis of the strands. The hydrogen bonds are formed between guanine and cytosine and between adenine and thymine. When pairing of bases between two strands (*e.g.*, in DNA) occurs, the two strands are said to be complementary to each other.

Ribonucleic acids RNA occur in both the nucleus and cytoplasm of all cells. RNA is synthesized in the nucleus under the supervision of DNA. A section of DNA double helix opens up and a complement to it is synthesized that contains ribose instead of deoxyribose. This new segment then separates as RNA (Fig. 19.12). The RNA molecule has only one strand. RNA contains the pyrimidine uracil in place of thymine in DNA.

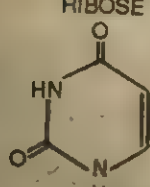
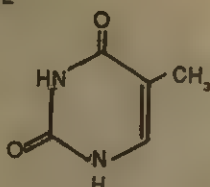
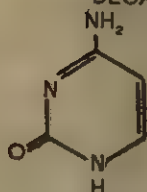
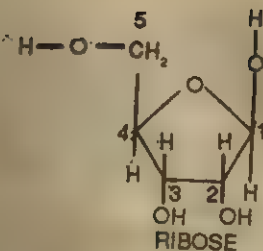
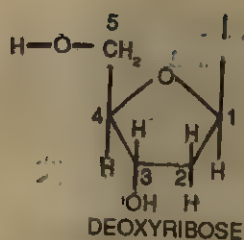
A section of DNA serves as the pattern for the synthesis of each RNA. The RNA migrates out of the nucleus into the cytoplasm of the cell. Three distinct types of RNA occur in the cells of higher organisms.

19.5.2 Biological Functions of Nucleic Acids

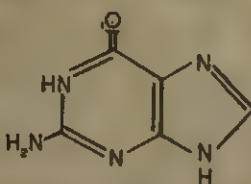
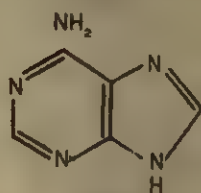
The two important functions of DNA are: (1) Replication and (2) Protein synthesis.

DNA is sometimes called the master molecule, since it plays a key role in life processes. It provides information and instructions as to what proteins are to be synthesized, *i.e.*, it controls the synthesis of proteins.

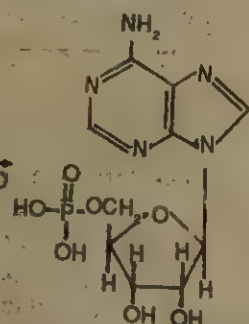
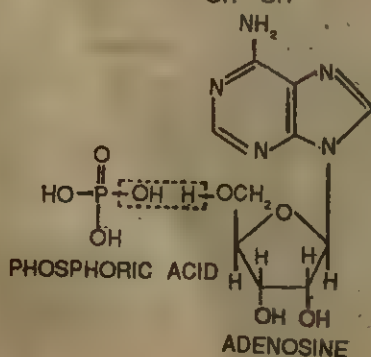
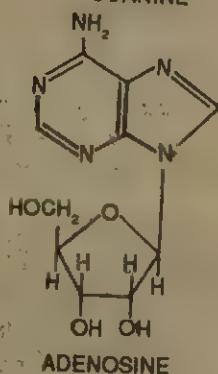
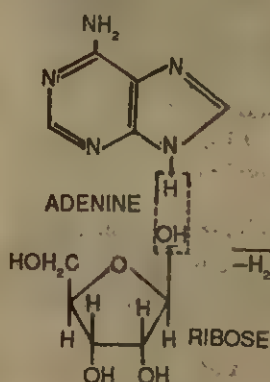
The DNA in the cell, has the property of precise self- replication. This property of DNA forms the basis for the reproduction of a complete animal or plant, *i.e.*, the transmission of hereditary characteristics from one generation to another. DNA can undergo mutations, *i.e.*, can undergo alteration in its nitrogenous base arrangement. This can happen by the action of X-rays, γ -rays and certain chemicals. As a result of mutations,

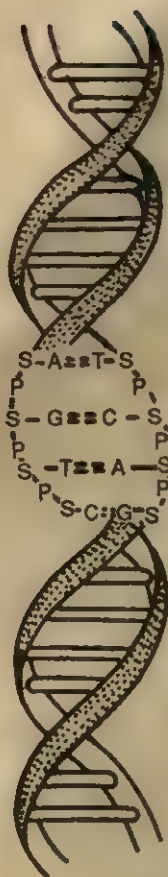


(PYRIMIDINE BASES)

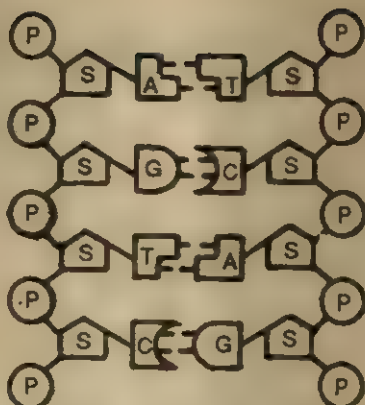


(PURINE BASES)

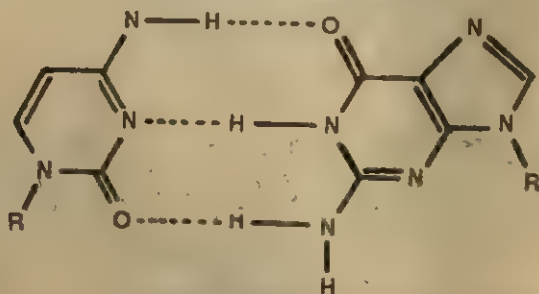




- (P) PHOSPHATE
- (S) SUGAR (DEOXYRIBOSE)
- (A) ADENINE
- (T) THYMINE
- (G) GUANINE
- (C) CYTOSINE

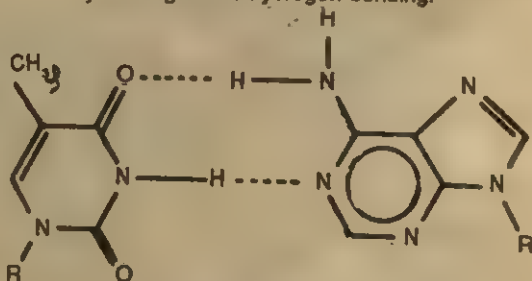


A representation of a portion of DNA. The bases adenine-thymine and guanine-cytosine are paired together with hydrogen bonds.



Cytosine-guanine hydrogen bonding.

The double helix in the DNA. The sugar phosphate chain provides the backbone of each strand.



Thymine-adenine hydrogen bonding.

Fig. 19.11

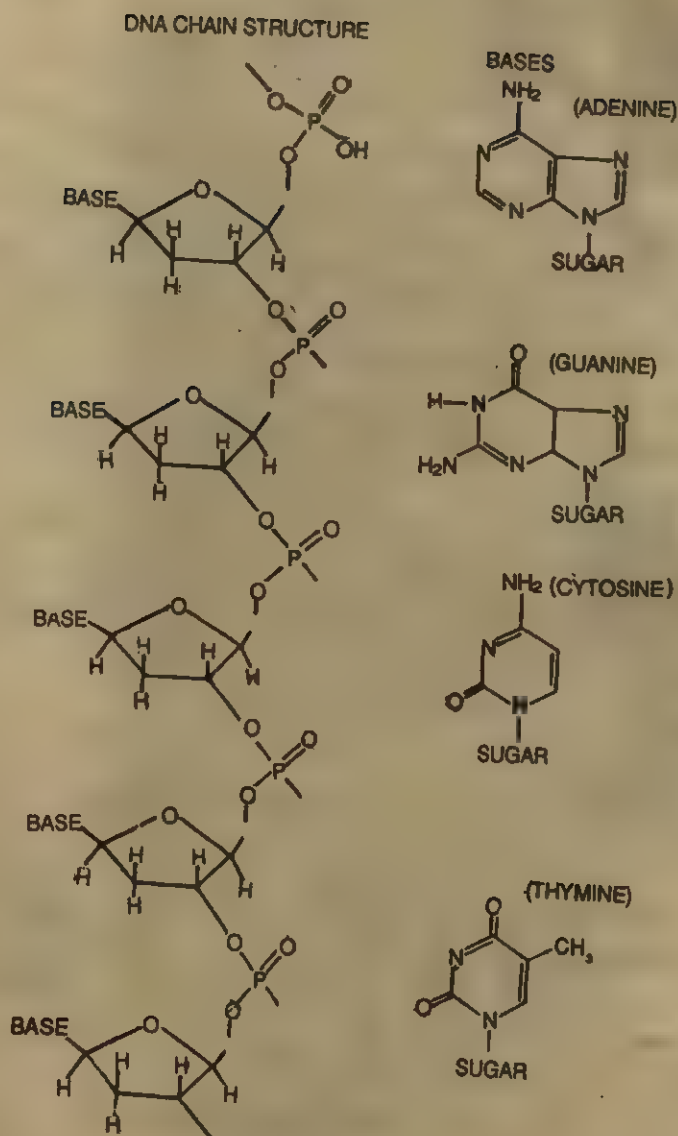


Fig. 29.11a Schematic structure of a single DNA chain. the four bases are shown are at the right.

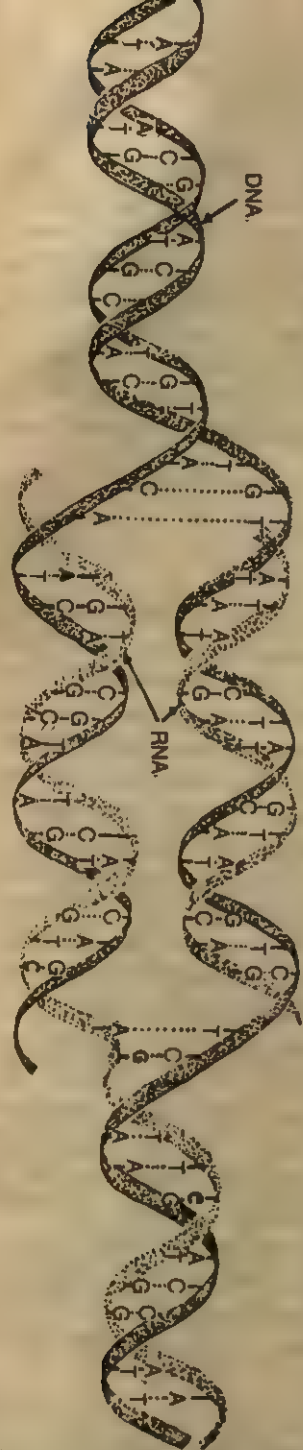


Fig. 19.12 Formation of RNA

structural and functional characteristics of a given species can change substantially.

Replication (Copying) of DNA

Cell division (undergo mitosis) is necessary for the growth and maintenance of each organism and for the formation of new organism. During cell division the two strands of DNA separate. Each daughter cell receives one of the two nucleic acid strands. Even though the two strands are not similar, they each contain the information necessary to remake the original dihelical structure. Here each strand serves as a pattern or template for the formation of two new strands which will be identical with that originally present in the parent cell (Fig. 19.13). This is because of the base pair specificity (*i.e.*, T with A and C with G). Thus, the exact sequence of bases in the DNA molecule can be retained from parent to daughter cell and through many generations. All the necessary information required for the growth and proper maintenance throughout the life of the cell, is stored in DNA molecule.

The following three types of RNA molecules are important in protein synthesis:

1. Messenger RNA (m-RNA)
2. Ribosomal RNA (r-RNA) and
3. Transfer RNA (t-RNA)

The m-RNA is a complementary copy of a portion of one strand of given DNA molecule. It carries the message given by a DNA molecule for specific protein synthesis. The r-RNA provides the site for protein synthesis in the cytoplasm.

The t-RNA is responsible for the transport of a specific amino acids to the site of protein synthesis. A little more than twenty different types of t-RNA have

been identified, each of these t- RNA molecules is specific for the transfer of one amino acid.

Protein Synthesis

DNA serves as an instructions manual for all protein synthesis in a cell but DNA does not furnish this information directly to the cell. It always works through m-RNA (present in the nucleus) whose function is to transcribe (rewrite) the information and make it available to the ribosomes (present outside) of the cytoplasm. Here it furnishes the information for producing the proper amino acid sequence to make a protein (Figs. 19.14 and 19.15). The m-RNA is then able to call up t-RNA molecules, each of which transport an amino acid to the site of protein synthesis. The system of replication, transcription and translation can be summarized.



The Genetic Code

The code (set of directions) that determines the exact sequence of amino acids in the protein synthesis is stored in the chromosomal DNA. It is always available in a well defined pattern of base molecules on the double helix of DNA. A group of three (triplet) base molecules in a DNA strand creates a situation where a complementary set of base molecules appear in the m-RNA formed on it. This triplet or codon on the m-RNA must be matched by a complementary triplet called an anticodon in t- RNA. The specific t-RNA with this anticodon carries a specific amino acid to the site of protein synthesis. Each segment of the DNA molecule which codes for a complete protein is called a gene. The DNA present in human cell contains about 5-50 billion nucleotide bases coding for nearly one million genes.

Nirenberg, Holey and Har Govind Khorana, through their studies aimed at relating specific

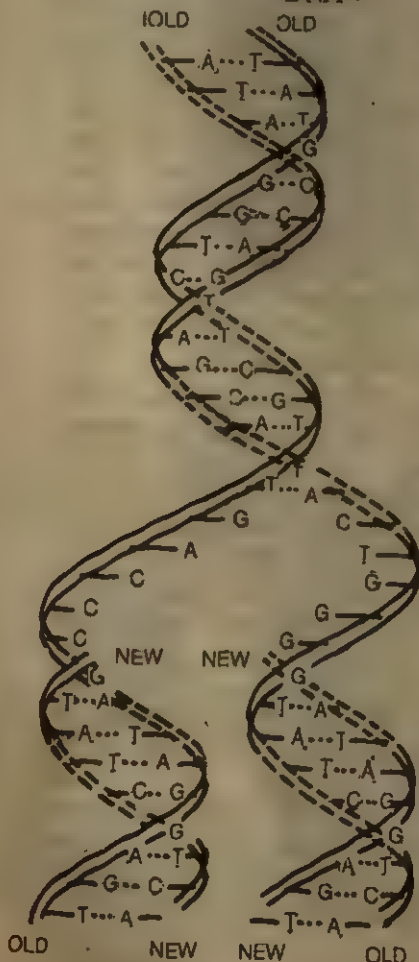


Fig. 19.13 Replication of DNA

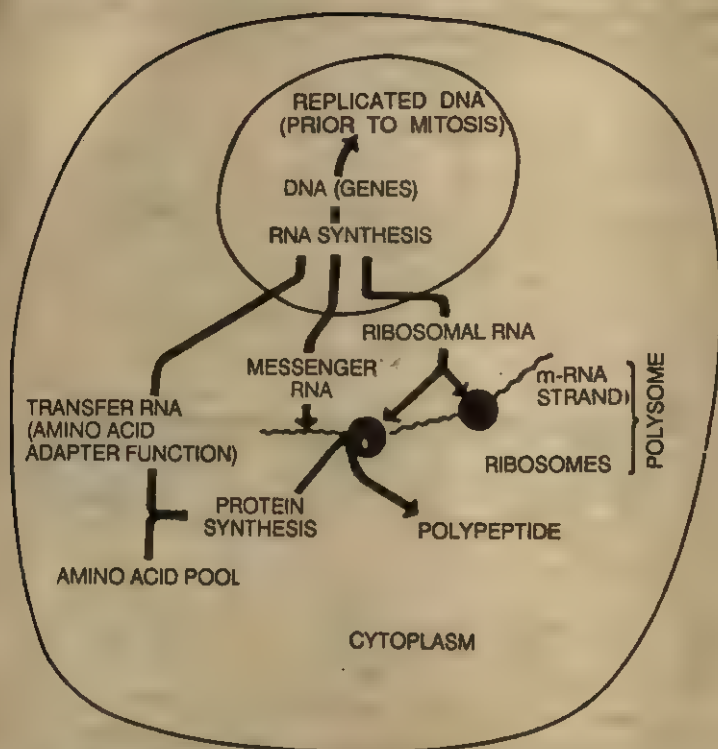


Fig. 19.14 The relation of DNA to various RNAs and protein synthesis.

codons to specific amino acid units have arrived at the genetic code given in Table 19.5 The significant features of the code are as listed below:

- o There is more than one triplet code for the amino acids.
- o The first two letters of the codon are most significant. The third letter varies.
- o There are several codons that do not represent any amino acids. Although they are referred to as nonsense codons, these seem to play a role in starting and terminating protein synthesis.
- o The various codons direct the same protein synthesis, whether in bacteria, plants, lower animals or humans.

The genetic code is presented in Table 19.5.

19.5.3 Viruses

Viruses cause the diseases such as *common cold*, *poliomyelitis*, *measles*, *small pox*, *rabies*, *influenza*, *mumps*, etc. Such diseases among human beings result from the formation of large number of virus

molecules from a few of these molecules when they are in the suitable environment in the human body. Viruses which infect bacteria are called bacterio-phages.

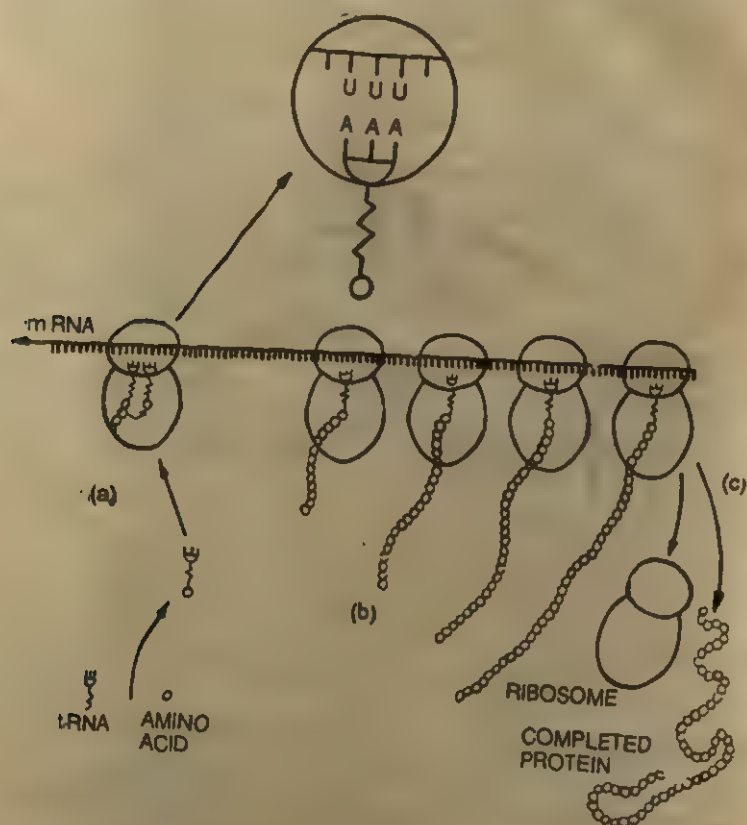


Fig. 19.15 Mechanism of protein synthesis (a) Through the action of an enzyme, at-RNA molecule brings a single amino acid to a site on a ribosome. The anticodon of the t-RNA AAA as shown must be complementary to the codon of the m-RNA (UUU). The amino acids join the chain as shown, the chain moves from the t-RNA on the left to the one on the right. (b) As the ribosomes move along the m-RNA strand, more and more amino acid units join through the proper matching of t-RNA molecules with the code on the m-RNA. (c) When the ribosome reaches the end of the m-RNA strand, it gets disconnected and releases the completed protein. The ribosome is free to repeat the process.

TABLE : 19.5 The genetic code

		Second base							
		U		C		A		G	
First base U	UUU	} Phe	UCU	} Ser	UAU	} Tyr	UGU	} Cys	
	UUC		UCC		UAC		UGC		
	UUA		UCA		UAA		UGA		
	UUG		UCG		UAG Nonsense		UGG Trp		
C	CUU	} Leu	CCU	} Pro	CAU	} His	CGU	} Arg	
	CUC		CCC		CAC		CGC		
	CUA		CCA		CAA		CGA		
	CUG		CCG		CAG		CGG		
A	AUU	} Ile	ACU	} Thr	AAU	} Asn	AGU	} Ser	
	AUC		ACC		AAC		AGC		
	AUA		ACA		AAA		AGA		
	AUG Met		ACG		AAG Lys		AGG Arg		
G	GUU	} Val	GCU	} Ala	GAU	} Asp	GGU	} Gly	
	GUC		GCC		GAC		GGC		
	GUA		GCA		GAA		GGA		
	GUG		GCG		GAG Glu		GGG		

Note : The symbols Phe, Thr, Gly, etc., represent aminoacids.

Viruses are the lowest form of life and are much smaller than bacteria. They are infectious in nature. They cause many diseases among plants and animals.

Viruses have a capacity to reproduce but they lack the capacity of multiplying themselves as cells. Because of this property, they can also be considered as living organisms. They first attack the host cells and try to control the reproductive machinery of these cells. Here, they start multiplying, and thus, destroying the old and new host cells.

The viruses are one kind of a giant molecules. They have the remarkable power of causing other molecules identical with themselves to be formed. They are no more than a protein coating wrapped around a nucleic acid (RNA and DNA) core. The RNA is infected by some viruses such as polio virus and tobacco mosaic virus (TMV). Bacteriophages, herpes virus and SV 40, polyoma virus (cancer causing) attack the DNA molecules.

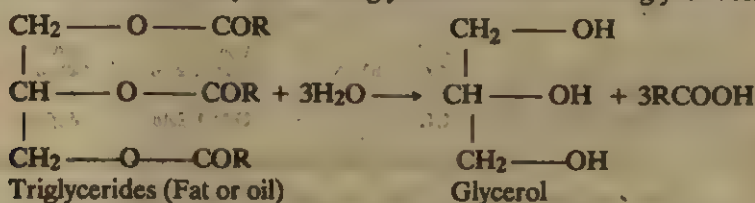
The electron microscope has made it possible to see and photograph virus molecules. Ordinary microscope cannot serve the job. They are too small to be seen.

19.6 LIPIDS

Lipids are high hydrocarbon content molecules which are essential constituents of all plant and animal tissues. Cell membranes and brain nervous tissues are particularly rich in lipids. The lipids present in biological tissues may be extracted with non-polar 'fat' solvent. The lipids are a heterogeneous group of organic compounds. Lipids include fat and oils (fatty acids esters), steroids and certain compound lipids such as phospholipids. They are classed together because of their solubility in the so called fat-solvents such as, benzene, ether, chloroform, carbon tetrachloride, etc. Lipids are generally insoluble in water. Waxes, triglycerides and phospholipids are the important naturally occurring lipids.

Unlike polysaccharides and proteins, lipids are not polymers, i.e., their molecular masses are relatively low:

Fats and oils are esters of glycerol (a trihydroxy alcohol) and fatty acids. The triesters of fatty acids with glycerol are known as triglycerides.

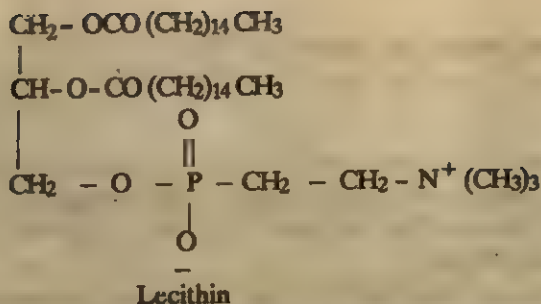


In fats and oils (triglycerides), the acid component of the esters may be saturated or unsaturated. We call a lipid a fat if it is a solid at 298K and an oil if it is a liquid at the same temperature. As the lipids from animal sources are generally solids, these are referred to as animal fats. Lipids obtained from plants are usually liquids at room temperature, and therefore, referred to as vegetable oils. This is because fats contain a greater proportion of saturated fatty acids, whereas oils contain more of unsaturated fatty acids.

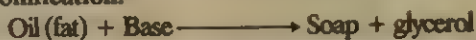
Vegetable oils can be hydrogenated to solid fats. Some of the acids present as esters in fats and oils are given below:

Name	Structural formula
Palmitic	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
Stearic	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
Oleic	$\text{CH}_3 - (\text{CH}_2)_7 - \text{CH} = \text{CH} - (\text{CH}_2)_7 - \text{COOH}$
Linoleic	$\text{CH}_3(\text{CH}_2)_4\text{CH} = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH} - (\text{CH}_2)_7 - \text{COOH}$
Linolenic	$\text{CH}_3\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH} =$

In phospholipids, one of the glycerol hydroxyl groups is esterified with a phosphoric acid derivative while the other two hydroxyls are combined with fatty acids. Thus, the phospholipid, lecithin has the structure:



Oils and fats can be hydrolyzed by alkali. The alkaline hydrolysis of fat is called saponification.



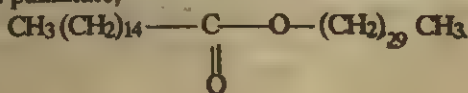
Soap is a mixture of the sodium or potassium salts of long chain carboxylic acids - such as, oleic ($\text{C}_{17}\text{H}_{33}\text{COOH}$), stearic ($\text{C}_{17}\text{H}_{35}\text{COOH}$) and palmitic ($\text{C}_{15}\text{H}_{31}\text{COOH}$). These are obtained from plants or animals. Soap is manufactured by boiling tallow (storage fat of cattle and sheep) or vegetable oil such as coconut oil with sodium or potassium hydroxide. Potassium soaps are milder than sodium ones, so potassium hydroxide is the alkali used in the manufacture of toilet soap. Sodium soaps have limited solubility in water and can be obtained as solid cakes. Potassium soaps are more soluble in water and are used as gels in shampoos and shaving creams.

Phospholipids are abundant in cell membrane, liver, brain and spinal tissues. They play an important part in many metabolic processes.

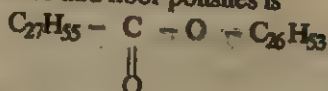
The presence of various lipids, along with a specific protein, impart unique structures to cell membranes so that they can do their functions effectively. Proteins in membranes help in carrying ions and molecules in and out of the cell. The cell membranes are perfect and selective barriers, which allow the nutrients to enter and the waste products to leave the cell.

Steroid lipids possess a characteristic cyclic structure, called a steroid nucleus. Cholesterol is the most abundant steroid in the human body. Some investigations indicate that there is a correlation between the cholesterol level in the blood and certain types of heart disease. Investigations are being carried out to see if reducing the blood cholesterol level by dietary precautions or by use of anticholesterol drugs will reduce the incidence of heart disease. Some steroids also act as vitamins and hormones.

Waxes are high molecular mass esters - of long chain fatty acids and long chain alcohols. For example, bee's wax, from honey comb of the bee is chiefly myricyl palmitate,



Carnabua wax, used in auto and floor polishes is



They are widely distributed in plants and animals where they frequently serve as protective agents. Wax coating protects surfaces of many plants leave from water loss and attack by micro-organisms.

19.7. CELL DEFENCE

The essential function of the immune system is defence against infection. The overall effect of the mechanisms employed by the host to fend off infection is summarized as host defence. The impact of mechanisms employed by the parasite that causes disease is termed as virulence. Antigens are macromolecules which upon administration stimulate antibody formation which specifically combines with them. They may be proteins (mostly), polysaccharides, glycoproteins, etc. The antibody specific globulins are called immunoglobulins. A few days after injecting the antigen, the antibody level rises, reaches a peak and then falls. This is known as primary response. Second exposure to the same antigen results in antibody formation faster and in higher titre.

When microbes enter the body, defence operations come into play.

1. Non specific humoral factors

Lysozyme, a low molecular mass basic protein, is most widespread bactericidal enzyme. It splits the exposed peptidoglycon wall of the SUSCEPTIBLE bacteria. It is present in serum, tears, etc. Oppsonins $\alpha_2\text{H}$ glycoproteins act by enhancing phagocytosis. Interferon, a glycoprotein, inhibits viral proliferation in the cells.

2. Specific response

(i) **Humoral Immunity** : Antigen on entering the body, evokes antibody synthesis which are then released into the blood and other body secretions. These antibodies act by neutralizing the bacterial toxin or by coating the bacteria and enhancing their phagocytosis by the phagocytes. This humoral antibody response is 'B' cell (Bursa derived Lymphocyte) function.

(ii) **Cellular Immunity** : Sensitised lymphocytes are produced which themselves are the effectors of cell mediated immunity. This is 'T' cell (Thymus derived Lymphocyte) function.

19.7. Immunity

(i) **Passively acquired immunity**: Administration of preformed antibody (Ab) from another individual of same (homologous) or different species (heterologous) affords immediate protection against the infection. Since these antibodies are progressively catabolized, the immunity is short lived. Pooled human γ -globulins are useful for temporary protection against measles, rubella, etc. Heterologous γ -globulins (produced in animals) are widely used for temporary prophylaxis against diphtheria, tetanus, etc.

(ii) **Actively acquired immunity**: Immunity actively induced by administering the pathogen or its products is long lasting, more effective and without the risk of hypersensitivity. The body actively participates in this humoral response.

19.7. Immunization

Prophylactic immunization is done for the prevention of the communicable diseases. The vaccines may be

(1) **Live**: Attenuated organism are used, *e.g.*, for small-pox poliomyelitis (Sabin) tuberculosis (B.C.G.) *etc.*

(2) **Killed organisms** are used for typhoid (T.A.B.) pertusis, *etc.*

(3) **Detoxified toxin (toxoids)** are used for tetanus, diphtheria, *etc.*

Adjuvants like alum are used to make the antigen more immunogenic and allowing slow and prolonged release of the antigen.

19.7.3 Medicines

Antimicrobial drugs are chemicals, which inhibit the growth of the micro-organisms while being tolerated by the host. They act by interfering with cell wall synthesis, protein synthesis, nucleic acid synthesis and intermediary metabolism of the microbe. This inhibitory effect may be reversible (*bacteriostatic*) or irreversible (*bactericidal*). Some inhibit the cell wall synthesis, *e.g.*, penicillin, bacitracin, cephalosporins, *etc.* inhibit the synthesis of peptidoglycon. They are effective only on the growing cells.

.... Some increase the cytoplasmic membrane permeability which results in increased leakage of essential metabolites, *e.g.* polymyxin, amphotericin B, *etc.*

.... Some inhibit nucleic acid synthesis, *e.g.*, greseofuluin, rifampine, *etc.*

.... Inhibition of RNA translation results in the inhibition of protein synthesis, *e.g.*, tetracycline, chloramphenicol, *etc.*

.... Inhibition of metabolic enzymes is achieved by metabolic antagonists. These compounds resemble their natural substrate.

SELF ASSESSMENT QUESTIONS

Multiple Choice Questions

19.1 Put tick (✓) mark against the most appropriate choice.

- (i) Disaccharide present in milk is
(a) sucrose (b) lactose (c) maltose (d) cellulose
- (ii) Which of the following monosaccharides is a pentose ?
(a) glucose (b) fructose (c) sucrose (d) ribose
- (iii) Cane sugar on hydrolysis gives
(a) glucose and maltose (b) glucose and lactose
(c) glucose and fructose (d) only glucose.
- (iv) Which of the following bases is not found in DNA ?
(a) thiamine (b) uracil (c) guanine (d) cytosine
- (v) Which of the followings are not associated with fibrous proteins ?
(a) hair (b) nail (c) muscle (d) brain
- (vi) Which of the followings is not a macromolecule ?
(a) proteins (b) nucleic acids (c) enzymes (d) lipids
- (vii) Which of the following compounds do not belong to lipids ?
(a) wax (b) fat (c) phospholipids (d) carbohydrates

- (viii) Which of the following compounds is not a protein ?
 (a) myoglobin (b) lysozyme (c) keratin (d) dextrin
- (ix) Which of the followings macromolecules do not contain nitrogen ?
 (a) proteins (b) enzymes (c) carbohydrates (d) nucleic acids
- (x) Which of the followings is associated with insulin ?
 (a) Frederick Sanger (b) Linus Pauling (c) H.G. Khorana (d) Fischer

19.2 Fill in the blanks :

- (a) Ribose and deoxyribose are called _____
 (b) An example of aldohexose is _____
 (c) Glucose and _____ are combined together in lactose
 (d) _____ is a combination of fructose and glucose.
 (e) Simple fats and _____ are esters of _____ and fatty acids.
 (f) Lipids which are _____ at room temperature are also called fats.
 (g) Cholesterol contains the _____ nucleus
 (h) Proteins are polymers of _____
 (i) The secondary structure of protein is determined by _____ which stabilizes the peptide chain.
 (j) Denaturing is accompanied by a loss of _____ activity.

19.3 Mark true (T) or false (F) against the following statements.

- (i) Cellulose is a monosaccharide.
 (ii) Fats are ordinary high polymers.
 (iii) Amino acid units are polymerized by peptide links
 (iv) Starch is a macromolecule consisting of β -glucose units.
 (v) The proteins are the addition polymers of amino acids.
 (vi) The secondary structure of protein is determined by hydrogen bonds which stabilize the peptide backbone into helical sheet or coil shapes.
 (vii) The pleated sheet conformation occurs widely in globular proteins.
 (viii) Alteration of tertiary structure or gross shape of protein is called denaturation.
 (ix) Enzymes are protein catalysts.
 (x) Enzymes are unusual catalyst in their high degree of specificity and efficiency.
 (xi) Nucleic acids are polymers consisting of nucleosides.
 (xii) Depending upon the pentose involved, there are two major classes of nucleic acids RNA and DNA.
 (xiii) Polymers serve as sites of protein synthesis.
 (xiv) Fats are absorbed chiefly as fatty acids, glycerol or monoglycerides, and are reesterified to triglyceride in the intestinal mucosal cells.
 (xv) Cell membrane is made of lipids.

19.4 Match the statements/words in column B against the words in Column A.

Column 'A'

1. Lecithins
2. Fatty acids
3. Cytoplasm
4. Ribose
5. Deoxyribose
6. Hydrolase
7. Condensation
8. Glycine
9. Thymine
10. Vitamins

Column 'B'

- (a) Triglyceride
- (b) RNA
- (c) Cell
- (d) Phospholipid
- (e) Enzyme
- (f) Pyrimidine
- (g) DNA
- (h) Amino acids
- (i) Coenzymes
- (j) Proteins

SHORT ANSWER QUESTIONS

19.5 Give answers of the following questions briefly :

1. Name the products which maltose, sucrose and lactose give on hydrolysis.
2. What is photosynthesis ?
3. What is a glycoside bond ?
4. What is saponification ?
5. What is hydrogenation ?
6. Translate the following base sequence abbreviations
 (a) A-C-G-U and (b) T-A-C-G
7. Giving the source, state some of the important uses of the followings :
 (a) starch (b) cellulose
8. Differentiate between an amide and peptide bond.
9. What are the important functions of proteins in the body ? Give illustrations.
10. Name the process which is related to unfolding to peptide chain. What does happen after the peptide chain unfold ?

11. How does DNA differ from RNA ?
12. To which class of the compounds the following compounds belong Guanine, thymine, uracil, triglyceride, wax, maltose, sucrose, invertase, yeast, pepsin, galactose, lecithin, cholesterol, cytosine.
13. What is the nature of bond in DNA ?
14. What will be the base sequence for the complementary RNA strand when the DNA base sequence is as given, A-T-G-C-T-A-T-A.
15. Name the products which are produced when wax is hydrolyzed ?

TERMINAL QUESTIONS

- 19.1 What is a cell ? Give its characteristics. What are building materials of cell ?
- 19.2 (a) What are carbohydrates ? How are they classified ?
(b) Is the name representative of their properties ?
- 19.3 What is a disaccharide ? How does it differ from polysaccharide ?
- 19.4 What role do carbohydrates play in living systems ?
- 19.5 What are lipids ? Mention the role they play in body functioning ?
- 19.6 (a) What are proteins ? Do they have amide linkages ?
(b) Describe the primary and secondary structures of proteins.
(c) What is meant by the term 'denaturation of a protein' ?
- 19.7 What are nucleic acids ? Do they differ from proteins in their chain structure ?
- 19.8 (a) What do the terms RNA and DNA stand for ? Point out the difference between the two.
(b) Mention three types of RNA molecules in a cell. Give function of each.
- 19.9 Describe briefly the double helix structure of DNA. Give the functions of DNA.
- 19.10 Name the enzymes useful for the fermentation of starch to alcohol.
- 19.11 Pick out the naturally occurring compounds from the followings :
starch, cellulose, α -amino acids, uracil, thymine, PVC, teflon polythene and urease.
- 19.12 Define the following terms :
(a) lipid (b) nucleic acid (c) carbohydrate
(d) enzyme, and (e) protein.
- 19.13 Describe the genetic code for nucleic acids. Define the terms gene, triplet, codon and anticodon.
- 19.14 (a) Explain the essential difference between the following pairs of materials.
(i) a fat and a lipid (ii) a fat and an oil and (iii) a fat and a wax.
(c) Explain why do phospholipids dissolve readily in water than simple or mixed of glycerides.
- 19.15 Describe what is meant by each of the following terms :
(a) amino acids (b) peptide bond (c) polypeptide (d) protein (e) N-terminal amino acid (f) α -helix (g) denaturation (h) asymmetric carbon atom, and (i) chiral centre.
- 19.16 What is meant by the primary, secondary and tertiary structure of a protein ?
- 19.17 Describe briefly the meaning of each of the following terms as they apply to metabolism : (a) anabolism and (b) catabolism.
- 19.18 What are two types of nucleic acids ? List their principal components.
- 19.19 What are the principal functions of each of the followings in protein synthesis : (a) DNA (b) m-RNA and (c) t-RNA ?
- 19.20 What is virus ? How does it multiply and attack a human body ?

ANSWERS TO SELF ASSESSMENT QUESTIONS

- 19.1 (i) b (ii) d (iii) c (iv) b (v) d (vi) d (vii) d (viii) c (ix) a.
- 19.2 (a) Pnetose, (b) glucose (c) galactose (d) sucrose (e) oils, glycerols (f) solid (g) steroid (h) amino acids (i) H-bonding, and (j) biological
- 19.3 (i) F (ii) F (iii) T (iv) F (v) F (vi) T (vii) F (viii) T (ix) T (x) T (xi) F (xii) T (xiii) T (xiv) F (xv) F
- 19.4 1 (d) 2 (a) 3 (c) 4 (b) 5 (g) 6 (i) 7 (j) 8 (h) 9 (f) 10 (i)
- 19.5 1. (i) Maltose + water \longrightarrow glucose and glucose
ii) Sucrose + water \longrightarrow glucose and fructose
iii) Lactose + water \longrightarrow glucose and galactose
2. Photosynthesis is a complex series of chemical reactions. In the sunlight chlorophyll absorbs energy. Photolysis of water produces hydrogen which can reduce carbon - dioxide giving glucose.
3. Linkage produced by the elimination of water when two simple sugar combines.
4. Saponification is the name given to the hydrolysis of fats or oils by a strong base.
5. It is a process of adding hydrogen across the double bond. Vegetable ghee is produced by hydrogenation.
6. (a) This is strand of RNA. A - C - G - U.
Adenine-Cytosine-Guanine-Uracil

(b) This is a strand DNA. T - A - C - G
Thymine-Adenine-Cytosine-Guanine

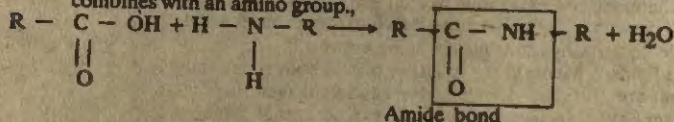
7. (i) **Starch** Source : Cereals, potatoes, legumes

Use : (1) source of food (2) Rich source of carbohydrate (3) manufacture ethanol

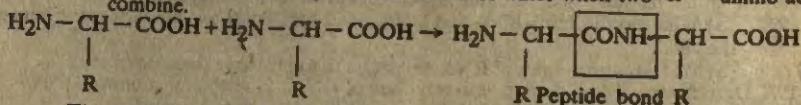
- (ii) **Cellulose** Source : Wool, wood, cotton

Uses : 1. Wood as source of cellulose is used for building and furniture (2) cotton is used in the manufacture of threads, fabrics, etc. (3) a good source of glucose (4) Esters of cellulose are used to make varnishes, many made fibers, etc.

8. An amide linkage is formed by the elimination of water molecule when a carboxylic acid combines with an amino group.



A peptide link is formed by the elimination of water when two α - amino acids combine.



The peptide bond (-CONH) involves the α - amino and α - carboxylic group of α - amino acids. More amino acids may be added to a peptide.

9. (i). Helps in storing oxygen in muscles until it is required for energy production - Myoglobin
(ii) A carrier of oxygen from lungs to various tissues through blood stream - Haemoglobin.
(iii) Helps in enhancing the rate of biochemical reactions - carbonic anhydrase, maltose, yeast etc.

10. Denaturation

It spoils the tertiary, structure of proteins, which results into a loss of biological activity. The protein becomes insoluble. Denaturation is caused by heat, acids, high salt concentration of heavy metals.

11. **DNA** = The nucleotide of DNA involves deoxyribose (sugar) and one of the four bases i.e., thymine (T) Cytosine (C), guanine (G) and adenine (A).

RNA = the nucleotide of RNA involves ribose (sugar) and one of the four bases i.e., uracil (U), cytosine (C), guanine (G) and adenine (A).

12. **Purine:** Guanine, cytosine

Pyrimidine: thymine, uracil

Lipid triglyceride, wax, lecithin, cholesterol

Proteins invertase, yeast, pepsin,

Carbohydrate maltose, sucrose, galactose.

13. The two strands of the DNA are held together by hydrogen bonds between base pairs. A is linked to T through two such bonds whereas G bonds to C with three hydrogen bonds.

14. Sequence of the other strand is TATAGCGC

15. Wax on hydrolysis gives long chain fatty acids and long chain alcohols.